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FOURIER TRANSFORM INFRARED SPECTROSCOPY

VOLUME I - TECHNICAL REPORT

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PREPARED FOR:

AIR FORCE ROCKET PROPULSION LABORATORY
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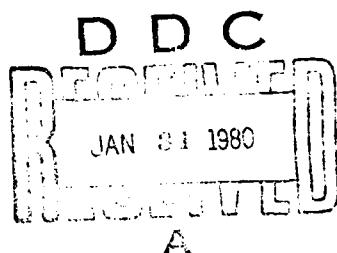
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FOREWORD

This report was submitted by Thiokol/Huntsville Division, Huntsville, AL 35807 under contract F04611-78-C-0027 Jon 573013LA with the Air Force Rocket Propulsion Laboratory, Edwards AFB, CA 93523

This report has been reviewed by the Information Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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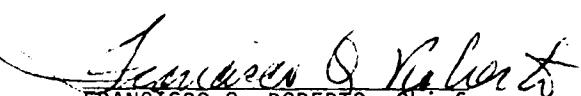
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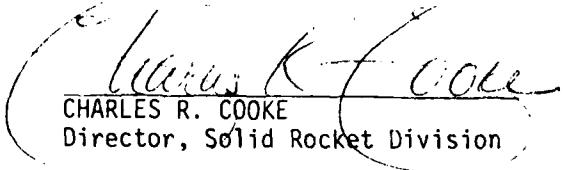
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This is the final report of a contract to establish the relationship between infrared spectra and propellant aging and to determine the applicability of this relationship to the prediction of service life of propellants.

Equipment for measurement of infrared spectra by both attenuated total reflectance and through transmission was identified, and procedures for sample preparation and testing were developed (cont'd)

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and demonstrated. Computer programs for reducing the infrared spectra data and statistically analyzing them were developed and made operational on the CDC 6600 computer at the Air Force Rocket Propulsion Laboratory.

Aging programs were conducted for two composite solid propellants, and the correlations between their infrared spectra and tensile properties as aging progressed were determined. Equations were established for the prediction of future tensile properties from spectral properties acquired during aging.

The major accomplishments of this project are the establishment of methods for predicting propellant tensile properties from infrared spectral data during storage and the development of procedures and computer programs for rapidly and economically processing large amounts of infrared data. The results of this project are a major step toward predicting the remaining shelf life of solid propellant rocket motors from infrared measurements using small amounts of propellant associated with them. Recommendations for application of these results and for improving and extending the developed methods are included in the report.

This report is composed of two volumes. Volume I contains the Technical Data and Volume II is the User's Manual.

Volume I

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TABLES (cont.)

FIGURES

FIGURES (cont.)

FIGURES (cont.)

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FIGURES (cont.)

INTRODUCTION

OBJECTIVE:

The objective os this project were to establish the relationship between infrared spectra and propellant aging and to determine the applicability of this relationship to the prediction of service life of propellant.

BACKGROUND:

In past programs, data that showed that changes in the chemical structure of the binder of a propellant could be correlated with changes in the mechanical properties of the propellant were obtained. It was also demonstrated that these changes to the chemical structure of the binder could be detected using infrared spectroscopy. Therefore, the changes in the infrared absorption characteristics of the binder are directly related to changes in the chemical structure and, hence, to changes in mechanical properties of the propellant. The purpose of this project was to demonstrate the feasibility of using Fourier transform infrared spectroscopy as a non-destructive tool to relate changes in binder structure to changes in mechanical properties of the propellant and eventually to use that correlation to predict the remaining service life of the propellant.

PROGRAM OUTLINE

The project consisted of two phases. These phases and the tasks that occurred under them are listed below.

Phase I - Analytical Development

Task 1 - Computer Program Development
Task 2 - IR Data Acquisition
Task 3 - Testing

Phase II - Service Life Prediction

Task 1 - Propellant Preparation
Task 2 - Aging and Testing
Task 3 - Prediction

During the Phase I studies, a computer program was to be developed to identify infrared frequencies in propellant binder that changed with the propellant's mechanical properties as functions of time and to identify those frequencies that were statistically and chemically relatable to the changes in mechanical properties. IR data acquisition techniques were to be refined so

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as to minimize interferences from propellant ingredients, especially ammonium perchlorate. The validity of the computer code and the data acquisition techniques were to be cross-checked with known results from on-going and previous programs (where specific data had been retained for this purpose).

In Phase II, recommendations were to be made to AFRPL for from one to four propellants for aging and testing. After AFRPL concurrence, this propellant(s) was to be manufactured for testing. These propellant(s) were to be aged (including gradient) for a specified time, and IR and mechanical property data accrued. These data were then to be used in the creation of mathematical technique to predict the remaining service life of the propellant. All data used in the prediction scheme were to be derived from the IR spectra of the aging propellant(s).

An over-view of the entire project is shown on Figure 1.

As originally planned the technical effort was to be complete in 18 months with an additional three months allowed for the final report cycle. This cycle was met, and all milestones were fulfilled.

Figure 1. Project Work Flow Diagram

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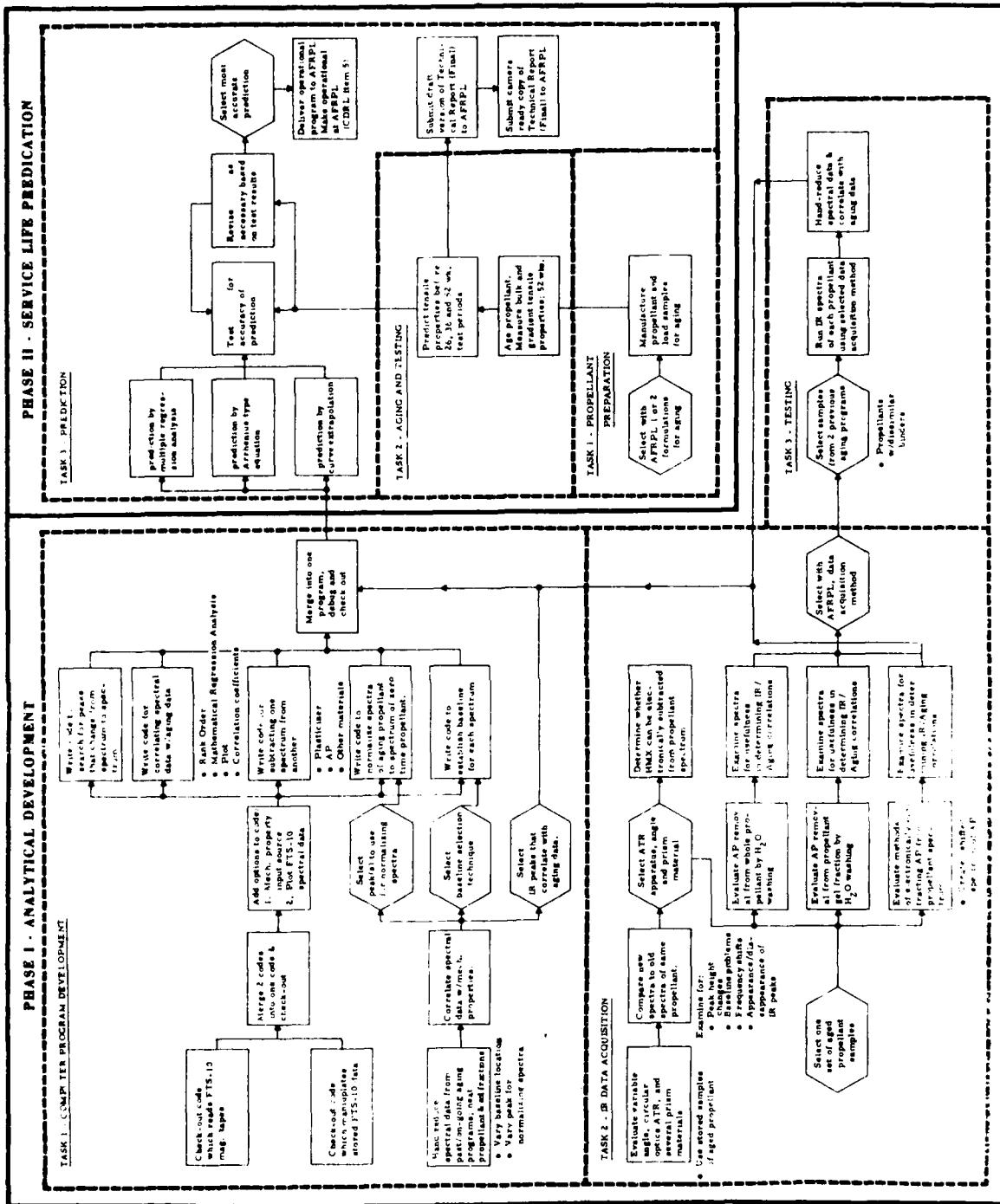
SUMMARY OF ACCOMPLISHMENTS

Infrared spectra of solid propellants were taken using an ATR technique, and the data were hand-reduced by a number of methods. Using these reduced infrared data, we correlated the heights of the various infrared peaks with propellant mechanical properties until we found a data reduction procedure that would give simple linear correlations of infrared peak height changes with corresponding changes in propellant mechanical properties caused by aging of the propellants. This data reduction technique was then mathematically modeled and used in developing a computer program to determine the height of each peak in an infrared spectrum.

A computer program was written to read FTS-10 spectral data tapes and from the data compute the spectra. The data reduction technique selected for measuring the heights of the infrared spectral peaks was included in the computer code and modified several times during the project to accommodate complex IR spectra. After computing the spectra, it was necessary to normalize them so that all spectra in a data set would be on the same basis and the peak height changes could be compared one to another among the spectra. Several peaks in the infrared spectra of propellants were evaluated as possible sites for normalizing, and the CH stretch region (2700 to 3100 wave numbers) was selected as that portion of the spectra that changed least due to aging of the propellant. Specifically, 2920 cm^{-1} was most useful for propellants that did not contain an ester plasticizer; and, for those propellants that did contain a plasticizer, 2850 cm^{-1} was preferred. After normalizing, peak heights are computed for all spectra in a data set and peaks are selected for a statistical analysis to show the correlation between peak heights and propellant mechanical properties changes. A separate program was written to accumulate the mechanical property data from user input and organize it into a form for the statistical analysis.

IR data acquisition techniques were studied, and several sample preparation procedures were found that yielded correlations of peak heights and mechanical property changes. Propellant spectra were measured using whole propellant (i.e., propellant that had not been treated in any way), propellant from which the ammonium perchlorate had been leached by water to remove the spectral influence of AP and "open up" the spectrum revealing more of the binder of the propellant, propellant sol fraction, and propellant gel fraction. Two ATR units were evaluated in the course of the program and a unit manufactured by Barnes Engineering Company was selected for standard use.

One of the critical factors found in this study of how the IR data are acquired was that whatever equipment and sample preparation procedures are used at the beginning of an aging program must be used throughout the aging program; otherwise the IR data will not have quantitative significance.

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When the IR data acquisition procedure was established, we tested
that procedure using two propellants aged as a part of this project. At
several intervals during the aging, several techniques for predicting the
aging characteristics of propellant were examined. The technique finally
selected for predicting properties of aging solid propellant involved estab-
lishing correlations between (1) peak height changes and propellant mechani-
cal properties, and (2) peak height changes with time, such that the predic-
tion was based solely upon infrared spectral changes and did not rely upon a
term in the equation that related propellant mechanical property changes
with time.

The major accomplishment in the program has been the development
of a computer code that will accept infrared spectral information from mag-
netic tape, reduce it, normalize it, calculate peak height, tabulate those
peak heights, and perform statistical simple linear correlations, multiple
linear correlations and multiple non-linear correlations. A method has
been identified for acquiring the infrared spectra of solid propellants so that
the spectra are quantitatively usable. Several methods for treating and pro-
pellants prior to taking the infrared spectra have been identified, and all
methods have shown correlations. Lastly, a technique has been developed
whereby a prediction of propellant mechanical properties to some future
time can be made mathematically using only infrared spectral information.

The results of this project are a major step toward predicting the
remaining shelf life of solid propellant rocket motors from infrared measure-
ments using small amounts of propellant associated with them.

TECHNICAL ACCOMPLISHMENTS

GENERAL REMARKS

The technical accomplishments of this report are presented below by phase and task of the program. The outline for the program is presented as a part of the introduction. Details of the experimental procedures developed during the course of the program are given in separate appendices located at the end of the report.

PHASE I - ANALYTICAL DEVELOPMENT

Task 1 - Computer Program Development

General Description of Programs

Two computer programs were written on this project. The first program was written to accept infrared data from magnetic tape, reduce the data, tabulate the heights of infrared peaks and correlate these data with propellant mechanical properties. The second of the two programs was one which tabulated the mechanical properties of a propellant. This physical properties master tape generator was an input to the infrared data reduction and analysis program. A general description of each of these programs, the development of each program and the capabilities and limitations of each follows.

Infrared Data Reduction and Analysis (E-490)

The infrared data reduction and analysis program accomplishes eight separate jobs. In order, these are:

1) Reads the FTS-10 spectral data tape.

2) Establishes the spectral baselines for the peak used to normalize the spectra.

3) Normalizes the spectra.

4) Computes baselines and peak heights for all peaks within the selected spectral range.

5) Tabulates spectral peak heights by file number.

6) Selects peaks for correlation with propellant properties.

7) Reads the propellant mechanical properties from the physical properties master tape generator.

8) Performs the statistical analyses that are called for.

Each of these subroutines in the program is treated separately below.

Physical Properties Master Tape Generator (E-410)

This program is for storing physical property data on propellant and it is the means for Program E-490 to access mechanical properties that the user wishes to have included in the correlations of spectral peak heights with propellant properties. Provisions are made for ten propellant properties, six of which have been pre-designated by headings. When a computer run is submitted, the data is stored on magnetic tape and is then accessed when needed by the E-490 program.

E-490 Program Development

FTS-10 Spectral Data Tapes Reading

An FTS-10 spectra file on magnetic tape consists of two records. The first record is a listing of the mathematics used to calculate the spectra from the binary bits that are stored on the tape as the second record of that file. An example of the information in the first record is given in Table 1. After having computed the spectrum, the computer prints out the spectrum in digital form. These data consist of a tabulation of wave numbers and amplitudes. Even though in later parts of the program (where it is computing peak heights), it is limited in the range of wave numbers that it treats. During this first part of the program, the computer establishes amplitudes for all wave numbers between the range 4004 and 393 wave numbers or whatever spectral range the user has elected to employ.

All spectra recorded on magnetic tape for use in this program must be absorbance spectra made between the spectral ranges of 4000 cm^{-1} to 400 cm^{-1}. Using the FTS-10 software with the FTS-10 spectrophotometer, the FTS-10 computer sets the parameters FLP and FFP one data point outside the two extremes such that the frequency of the first point in the spectrum will be in the order of 4004 cm^{-1} and the last data point in the spectrum will be approximately 393 cm^{-1}. This way if the spectra are collected in single precision, the number of data words in the record will be 468. The computer program E-490 has been coded to accept that number or a small number. This limit of 468 data words in the FTS-10 data tape requires also that the spectra be collected in single precision, i. e., the FTS-10 parameter WDS = SP. It was the practice during the FTS program to collect all the spectra with a resolution value of 8, i. e., a data word every 8 wave numbers. However, the resolution of the spectra may be changed at the user's discretion provided other changes are made in the FTS-10 collect parameters such that the number of data words does not exceed 468.

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Spectral Baselines Establishment

Before any quantitative information can be obtained from an infrared spectrum, one must know the height of the peak since the height of the peak is proportional to the transmitted radiation for the sample. In order to establish the height of a peak, it is imperative that a baseline be drawn beneath a peak such that the amplitude of the peak at this baseline is subtracted from the maximum amplitude of the peak and, thus, the height of a peak is known.

The entire scheme for using infrared data quantitatively depends upon the Beer-Lambert law which is expressed as follows:

$$kcd = \log_{10} i_0/i \tag{1}$$

In this equation:

i_0 = the incident radiation

i = the transmitted radiation

k = the absorptivity or extinction coefficient for a particular infrared peak in a particular compound

c = the concentration of the material being tested

d = the thickness of the sample

Establishing spectral baselines was one of the first problems tackled on the program. In order to keep the computer run time as short as possible and the programming as simple as possible, the first technique tried was a baseline which extended from 3100 to 2700 cm^{-1} and a second which connected 1800 cm^{-1} with 700 cm^{-1}; however, the precision of the peak height data calculated using this baseline was not nearly precise enough, so other techniques were tried.

In-hand reduction of an infrared spectrum, the usual technique for establishing a baseline, is to draw a line which connects the minimum on one side of a peak to the minimum on the other side of the peak. With a baseline drawn thusly, it is possible to calculate the height of a peak by merely subtracting the amplitude of the peak at the baseline from the maximum amplitude of the peak. This procedure worked well and the computer logic for accomplishing data reduction by this scheme was written. Later it became quite apparent that a minimum-to-minimum connector for baseline was not entirely adequate and there were some circumstances under which entirely false information

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was derived from using this baseline.

Figure 2 is a portion of a typical infrared spectrum showing the various baselines that the computer would draw depending upon instructions given to it. Take for example, peak A on Figure . Here the computer has drawn a minimum-to-minimum connector for that peak; and, using the equation for that line and the wave number at the peak, the computer is able to calculate the height of that peak. For this case the minimum-to-minimum connector is the proper one. Now look at peak B on that figure and observe that a minimum-to-minimum connector for peak B is not adequate. On the right side of peak B, i. e. , between peak B and peak C, the minimum is the correct point, but observe what happens when the computer searches for a minimum point on the left side of peak B. It finds a minimum near peak A and draws a line which cuts off a significant part of peak B such that an incorrect baseline for peak B is derived. This incorrect line is labeled (1) on the figure.

When this condition was detected, a new technique for establishing baselines was programmed. Basically, the computer searches for a tangent point along the left side of peak B. The new routine for establishing this tangent-to-tangent connector for a baseline proceeds as follows. The computer locates peak B and searches wave number-by-wave number down the right side of the peak until it reaches a minimum point; then retains that wave number and that amplitude. The computer then returns to the greatest amplitude in peak B and searches down the left side of peak B until it locates the minimum point, which in this illustration is the right side of peak A. The computer then calculates the slope of the line indicated as line (1) on the figure. It then indexes one wave number toward peak B and calculates a new slope. If that slope (line 2) is greater than the slope at line (1), the computer indexes one more wave number toward peak B and computes a new slope, shown as line (3) on Figure 2. If the slope of line (3) is greater than the slope of line (2), the procedure is repeated until the computer encounters a line where the slope is less than the slope of the previously computed line. In the illustration in Figure 2, the very next computation would yield a slope which was less than the slope of line (3). The computer would then select line (3) as the proper baseline and this, in fact, is the proper baseline for peak B. In order for the computer to know which side of the peak in the example peak B is apt to have a tangency baseline rather than a minimum baseline, the computer first selects the short side of the peak and holds that minimum point. It then goes to the long side of the peak and proceeds with the tangency baseline calculations.

Observe now the condition that exists with peak C in Figure 2. Here the short side of the peak is to the left and the computer selects the minimum along that line and searches the right side of peak C until it reaches a minimum. It then proceeds to apply the tangency baseline routine by indexing one wave number toward the peak and calculate the slope of the new line. In
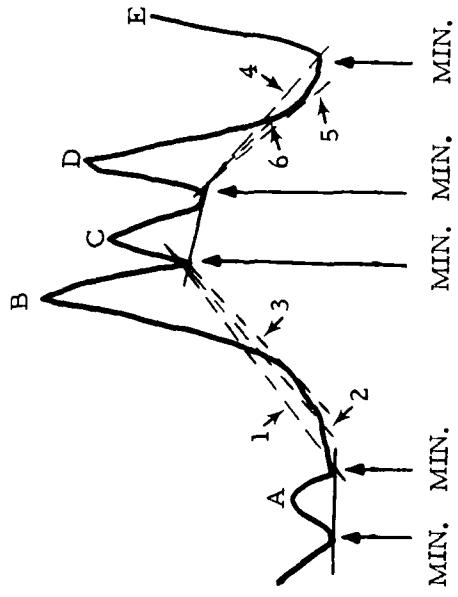
Figure 2. Portion of a Typical IR Spectrum Showing Various Baselines

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this instance, the new slope would have a lesser numerical value than the original slope so the computer would select the original line as is shown in the illustration.

The same search procedure is used for peak D in the Figure 2 illustration. Here the left side of peak D is short and the computer selects the first available minimum and that is to be one side of the baseline. It then searches the right side of peak D and finds the minimum and calculates the slope. This line is identified as line (4) in the illustration. It then indexes one wave number toward peak D and calculates a line which is identified as (5) in the illustration. The slope of this line is greater than the numerical value of the slope at line(4). It then indexes one more wave number toward peak D and establishes line (6) as the baseline and computes the slope of that line; however, the slope of line (6) is less than the slope of line (5), so the computer returns to line (5) and establishes that as the baseline for peak D. Again, this is the correct baseline for measuring the height of peak D.

Another interesting problem that presented itself was how to handle peaks in the infrared which should be measured from a common baseline rather than from a minimum-to-minimum connector or a tangent-to-tangent connector. This problem arose primarily from an instance where one peak grew in the infrared spectrum and a second adjacent peak diminished as the propellant aged, indicating a reaction product is formed while a reactant is disappearing. Figure 3 is an illustration of this phenomenon. It occurred quite in the spectra of TP-H8156 propellant, a carboxyl-terminated polybutadiene cured with an epoxide. There is a peak at approximately 1710 cm^{-1} that slowly disappears as the propellant ages. This is associated with unreacted carboxylic acid in the polymer. As the carboxylic acid disappears, a peak at approximately 1740 cm^{-1} grows; this is an ester peak which is the reduction product of the carboxyl with the epoxide.

It was felt that these two peaks really should be measured from a common baseline rather than from individual baselines in order to make the data more quantitative. To accomplish this, a new routine was written into the E-490 program and was called "common baseline" and is abbreviated COBASE. In order to establish a common baseline, the user designates to the computer those areas in the spectrum which are to be treated with this COBASE routine. In the Figure 3 example the user would enter the spectral limits of 1750 and 1700 wave numbers. Now the computer searches outside each of these limits until it finds a minimum and then draws the connector between these minima. It also applies the tangency baseline routine if this region of the spectra requires that type of baseline. As many as 25 peaks can be included in any one request for the COBASE routine.

In order to account for those conditions under which a peak almost totally disappears or ceases to become a peak, but merely a discontinuity or
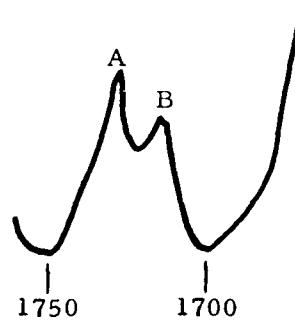
Figure 3. Portion of An IR Spectrum Showing the
Application of the Common Baseline Routine
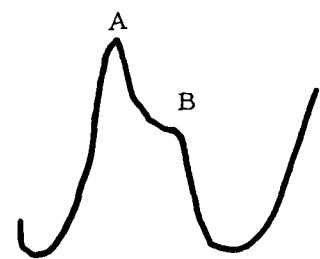
Figure 4. Portion of an IR Spectrum Showing A Peak
Reduced to a Shoulder on Another Peak

shoulder on a first peak, the computer has instructions to retain the wave
number of each peak in the COBASE area, using a spectrum which the user
decides is the best "picture" of the COBASE area. In all spectra of that data
set it goes to those two wave numbers and measures the height of whatever is
at that location whether it be an actual peak or merely a shoulder on the side
of another peak. This condition is illustrated in Figure 4. In this illustration
the shoulder designated as "B" is a reduced version of the smaller peak shown
in Figure 3. Here the computer has remembered the location of B in Figure 2
and is still computing the height of B even though it is no longer a peak as far
as the computer is concerned, because it does not go through a maximum as
A does.

Spectra Normalization

In order to have the infrared spectra quantitative, one must somehow
account for all the variables in the Beer-Lambert law, equation 1. In that
law the incident radiation becomes a constant in the computation of the spectra
from the reference and sample files. Absorption in the infrared spectrum of
a particular group in a molecule is a constant and so the extinction coefficient
is removed as a variable so long as one is observing identical peaks in a series
of spectra. Concentration can be accounted for by a process called normalizing.
Sample thickness is accounted for in the ATR unit because the penetration of the
infrared energy into the sample is a function of the angle of incidence of the
infrared light, the material being used as the IRE and the wave number being
examined so long as the same ATR unit and IRE are used, sample thickness is
a constant. This leaves the transmitted radiation as the measure of the amount
of material present in a particular sample when compared to another sample of
the same material.

In order to normalize one selects a peak in the infrared spectrum and
makes the assumption that the height of that peak does not change because of
the changes from sample-to-sample, in other words, this is a point of zero
change in the molecular structure of the material being tested. Now it is
recognized that zero change is probably an impossibility, but since we must
normalize, we must use the best approximation that we can and search for
a peak in the spectrum where there is as little change as possible.

A large number of infrared peaks were tried in the course of the pro-
gram and it was concluded after having the data reduced using a number of
normalizing peaks, that peaks in the CH_x region (2920 and 2850 cm^{-1}) were
best for normalizing. 2920 was used most frequently and on occasion, 2850
was used for normalizing. For those samples of propellant where the CH of
the ester is used as the plasticizer (a material such as DOA) it was found that
2850 cm^{-1} was a region where the CH of the ester does not interfere with the
CH_x of the polymer binder which does absorb strongly. Thus, any variation

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in the quantity of plasticizer presented to the infrared energy beam has little or no influence upon the normalization of the propellant sample spectrum. Where one is working with the gel fraction of propellant, where the DOA has been extracted, the peak at 2920 cm^{-1} is the most constant from sample to sample.

In using the E-490 program for IR data reduction, the user is given the option to select the normalizing wave number. The computer then goes to this designated location and searches $\pm$ 20 wave numbers, to account for some variation in the manner in which the spectra are collected, to find the maximum amplitude in that region. It identifies that amplitude, and then identifies the wave number at which that amplitude occurs. It proceeds through the baseline routine to establish the baseline for that peak and then computes the amplitude of that peak in the first spectrum of the data set.

Program E-490 then measures the amplitude of the normalizing peak in every other spectrum of the data set. Having established all normalizing peak heights, it then reviews the data and selects that spectrum which has the greatest peak height at the normalizing area. This is used as a computational standard for the remaining spectra. The greatest normalizing peak in a set of spectra is divided by the normalizing peak height of every other spectrum. This numerical value becomes the normalizing factor for the particular file. Every other amplitude in the file is multiplied by this normalizing factor so that now all of the spectral information from all files in the data set are on the same numerical basis and they all have been "normalized". An example of the type of information that is printed by the computer is given in Table 1. The computer then prints out the amplitude at each wave number for each of the normalized spectra. These normalized spectra will be plotted if the user chooses. All subsequent computations are made with this normalized spectral information.

It should be pointed out that the computer program normalizes by the procedure given above using the greatest normalizing peak height in a set of spectra. It does not use a standard peak height which would permit the comparison of spectra among data sets. The computer program permits the comparison of spectra within a data set only.

Peak Height Computation

Once all of the spectra in a data set have been normalized, the program computes the height of each peak within the spectrum. Starting at 3200 cm^{-1}, the computer searches for a maximum amplitude and then identifies that wave number. It then searches the left side of this located peak for the minimum point and then searches the right side for the minimum point. From these two points, it selects the long side and calculates the slope of the line connecting these two minima. Having done this, it proceeds through the tangency baseline selection routine and when it has located the proper baseline it then

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TABLE 1

EXAMPLE OF PRINTOUT, NORMALIZED AMPLITUDE INFORMATION

NORMALIZED AMPLITUDE INFORMATION -- FTIS FILE NO. 32

MAXIMUM AMPLITUDE NEAREST 2920.0 WN. = 0.2862854E+02

WAVE NUMBER AT MAX. AMPLITUDE = 2921.7649

CALCULATED BASELINE AMPLITUDE AT 2921.7649 WN. = 0.9963986E+01

PEAK HEIGHT AT 2921.7649 WN. (APNORM) = 0.1866455E+02

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calculates the amplitude on this baseline at the peak wave number. It subtracts this value from the maximum amplitude it identified in the first step and this new value then becomes "peak height". A summary of all of the steps involved in calculating a single peak height is given in Table 2. The computer proceeds through this routine for all IR spectral files in the data set.

In order to keep the run time of the program to a minimum, some restrictions were placed in the program to prevent the computer from examining peaks which amount to only spectral noise. Computation of peak height begins at a wave number of 3200 cm^{-1} and proceeds through 2700 cm^{-1}. This is the CH$_x$ region of the spectrum and is important in normalizing; also, in this region are some peaks which correlate with propellant mechanical properties. Between 2700 cm^{-1} and 1800 cm^{-1} there are no spectral features that are of interest. This region of the spectrum is flat and any small peaks that occur in this area are merely electronic noise. Beginning at approximately 1800 cm^{-1}, and proceeding through 700 cm^{-1}, is the "fingerprint" region of the spectrum which reveals a large amount of information concerning the chemical behavior of the binder within the propellant. The computer searches this entire region and identifies each peak in that region. Beyond 700 cm^{-1}, there are few peaks which might reveal something about changes in the composition of the propellant binder; and there is one very strong ammonium perchlorate absorption in this region.

The computer program has been written to allow up to 50 peaks per spectrum; thus, the data array for peak heights is quite large and very complex spectra can be handled by the computer.

Up to 30 spectral files can be treated in a single computer run. If the user finds a need for reducing more than 30 spectral files, it can be accomplished in two or more runs provided that in each computer run the largest spectrum in the entire data set is included in each run. Selecting the largest spectrum in a set of data can be accomplished merely by reviewing the spectral plots that were made by the infrared spectrophotometer. Having the largest spectrum included in each computer run is a necessity so that all of the spectra are normalized on the same single spectrum; thus, all the spectra, regardless of how many are comparable one with another because they have been normalized to the same single spectrum.

In this peak height calculation routine for the computer, the computer has not been instructed to distinguish between electronic noise and genuine peaks and it computes peaks regardless of how small they might be. In order to avoid correlation of peaks which are electronic noise with propellant mechanical properties, the computer at this point has been instructed to determine the "validity" of a peak. A "valid" peak is defined by a user input but defaults to 2% of the overall amplitude within a spectrum. The computer accomplishes this by identifying the maximum amplitude within each spectrum

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TABLE 2

SUMMARY OF COMPUTER STEPS TO

CALCULATE PEAK HEIGHT

1) LOCATE A MAXIMUM AMPLITUDE AND IDENTIFY WAVE NUMBER

2) SEARCH LEFT SIDE FOR THE MIN. POINT

3) SEARCH RIGHT SIDE FOR THE MIN. POINT

4) SELECT THE LONG SIDE

5) CALCULATE SLOPE OF LINE CONNECTING MINIMA

6) INDEX ONE DW TOWARD PEAK ON LONG SIDE, CALCULATE SLOPE

7) IS NEW SLOPE =, <, >,OR HAS SIGN CHANGED?

      IF =, STOP

      IF <,STOP, BACK-UP ONE DW

      IF >, REPEAT (6)

      IF SIGN OF SLOPE HAS CHANGED, BACK-UP ONE DW

8) WHEN TAN/MIN. ON LONG SIDE IS FOUND, CALCULATE EQUATION
FOR THE "BASELINE"

9) CALCULATE AMPLITUDE ON BASELINE AT PEAK WN (No. 1 ABOVE)

10) SUBTRACT (9) FROM (1). THIS VALUE IS "PEAK HEIGHT"

11) LOCATE NEXT MAXIMUM AMPLITUDE, ETC.---, TO END OF SPECTRUM

12) STORE DATA ARRAY

13) PRINT DATA ARRAY: PEAK NUMBER, DW, WN, PEAK HEIGHT,
                      BASELINE AMPLITUDE

and identifying the spectral minimum amplitude. It subtracts the minimum from the maximum and multiplies that value by 0.02 and any peak that has a height less than this value is considered to be non-valid. Valid peaks are denoted on the computer print-out by three asterisks (***). The validity of a peak is determined for each individual spectrum in a data set, not for the data set as a whole. In other words, the computer does not consider the maximum amplitude in the entire set of spectra and the minimum amplitude in the entire set, but determines validity for each individual spectrum. This means that a peak may be considered valid in one spectrum simply because of the maximum and minimum amplitudes in that spectrum permit it, and it may be considered invalid in another spectrum in the same data set. This has led to a few problems in the correlation of peaks with propellant mechanical properties. This problem will be discussed in the next section of the report. Table 3 is an example of the type of information that the computer prints concerning peak heights. Observe on that table that the computer keeps track of peaks by number; it also identifies the data word at which the peak occurs, the wave number in cm^{-1} at which the peak occurs, prints the height of the peak and the amplitude of the spectrum along the baseline. Notice in the example that peak numbers 2, 3, 4, and 7 are valid peaks while all the others are not. Table 4 is a summary of this discussion concerning the features and limitations of the computer program as it proceeds through the peak height calculation routine. One other piece of information appears in the Table 3 summary of peak heights and that is the notation "CB" which is a record of the peaks that were involved in the common baseline routine.

Peak Height Tabulation by Spectra File Number

After all peak heights have been computed for all of the files submitted in a run, the computer then tabulates these peak heights by data word and by spectral file number. Tabulation is made by data word rather than by wave number simply because if spectra are not made under exactly the same conditions then there can be a slight variation in the wave number, but provided the original conditions for collecting the spectra are not too different, the data word number will not change.

The wave number for any spectrum is determined by the computer when it goes through the original data reduction routine. In order to establish wave number, it must know the resolution element for the particular spectrum and this is accomplished by subtracting the frequency of the last point (FLP) from the frequency of the first point (FFP) to establish the precise range for a given spectrum. This spectral range is then divided by the number of data words in the entire spectrum and this value then becomes the resolution element. The computer identifies from the first record in a spectral file the frequency of the first point. It then subtracts the resolution element and that new value then becomes the wave number for the second data word. The resolution element is subtracted again, and this value becomes the third wave

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TABLE 3

EXAMPLE OF PEAK HEIGHT SUMMARY PRINTED BY COMPUTER

Fourier Transform Infrared Spectroscopy -- Normalized Peak Height Information: File Number 17

*** - Denotes a Valid Peak.

PEAK NUMBER	DATA WORD	WAVE NUMBER	PEAK HEIGHT	BASELINE AMPLITUDE
1	120	3083.8831	0.8718557	3.3381071
***2	130	3006.5447	1.0118046	5.9799166
***3	141	2921.4722	16.9562988	8.2677755
***4	150	2851.8674	9.6914034	7.1387053
5	162	2759.0o13	0.0860167	2.1017361
6	164	2743.5935	0.0843945	1.9475536
***7	294	1738.1921	2.6090755	4.6488113
8	298	1707.2568	1.5904989	5.1447935
9	307	1637.6521	1.7588291	5.0446281
10	311	1606.7166	0.9413185	5.5440369
11	314	1583.5151	0.3448792	5.7736874

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TABLE 4

SUMMARY OF COMPUTER PROGRAM PEAK HEIGHT

CALCULATION FEATURES AND LIMITATIONS

1) CALCULATES HEIGHT OF ALL PEAKS IN SPECTRAL REGIONS: 3200 TO 2700 cm^{-1} AND 1800 TO 700 cm^{-1}

2) DATA ARRAY ALLOWS UP TO 50 PEAKS/SPECTRUM

3) UP TO 30 SPECTRA FILES CAN BE TREATED IN ONE COMPUTER RUN

4) A "VALID" PEAK IS DETERMINED BY THE LENGTH OF ITS LONG SIDE, WHERE THE LENGTH OF THIS SIDE MUST BE (X) [(SPECTRAL MAX. AMPLITUDE) - (SPECTRAL MIN. AMPLITUDE)] WHERE (X) IS A DECIMAL FRACTION DESIGNATED BY THE USER. DEFAULT VALUE IS 0.02

5) VALID PEAKS ARE DENOTED BY ***

6) VALIDITY IS DETERMINED FOR EACH INDIVIDUAL SPECTRUM IN A SET, NOT FOR THE SET AS A WHOLE

number in the tabulation of the spectral information. Since wave numbers can change slightly from spectrum to spectrum depending upon the FFP and the FLP values, the decision was made that the computer would keep track of the spectral information by data word number. An example of the peak height tabulation provided by the computer is shown in Table 5.

In order to identify the wave number for a particular data word, one refers back to the tabulation for the peak heights in a particular spectrum. Table 3 is such a tabulation. Take, for example, data word 120 on Table 5 in file 17; that peak had a height of 0.872. Refer now to Table 3 and observe that data word 120 had a wave number of 3083.8831 cm^{-1} and a peak height of 0.8718557 (the computer rounds off the peak height values in the Table 5 tabulation to three places). Note also on Table 5 that file no. 17 did not have data words 115 and 117. These data words, however, did occur in file 29. One of them occurred in file 23, one occurred in file 35 and one occurred in file 41. Also, in the Table 5 tabulation, the information concerning the validity of a peak has been dropped out as has the information concerning the peaks which are involved in the common baseline routine.

The peak height tabulation summary was programmed as a convenience so that if the user did not wish to employ the statistical analysis routine in the program he could select peak heights from the Table 5 tabulation and perform his own statistical analysis using a procedure of his choosing. The original statistical analysis of the peak height and propellant mechanical property information was done in just this manner until the statistical analysis capability was programmed. Selected portions of the statistical analysis computer program used for this were later incorporated into E-490.

Peak Selection for Statistical Analysis

In order to determine whether peaks in the infrared spectrum correlate with changes in mechanical properties of propellant, it is first necessary for the computer to review the data and select those peaks that are to be correlated with propellant mechanical properties. Two criteria were established for selecting these peaks.

A) Is there a peak at a given wave number in every spectrum in the data set; and

B) Is each peak a valid one; i. e. , is its magnitude greater than 2% of the overall magnitude of the respective spectrum.

All peaks which meet these two criteria are employed by the computer in the statistical analysis.

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TABLE 5

PEAK HEIGHT TABULATION

FTIS ※※※※※※※※※ Peak Height Tabulation for all Requested Files ※※※※※※※※※

DATA WORD	FILE 11	FILE 17	FILE 23	FILE 29	FILE 35	FILE 41
115	0.0	0.0	0.0	0.234	0.071	0.096
117	0.0	0.0	0.054	0.066	0.0	0.0
120	0.846	0.872	0.0	0.0	0.927	1.042
121	0.0	0.0	0.996	0.938	0.0	0.0
129	0.0	0.0	1.407	0.0	0.0	0.0
130	1.119	1.012	0.0	0.982	0.960	0.961
132	0.314	0.0	0.0	0.0	0.0	0.0
141	16.956	16.956	16.956	16.956	16.956	16.956

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Very soon after writing these instructions into the E-490 program and having included a statistical analysis routine, it became apparent that the two criteria led to some problems when the computer performed the statistical analysis of the correlations between peak height changes and propellant mechanical property changes.

When the spectra of whole propellant are used AP and DOA peaks are always selected for the correlations routine. Some very strong correlations have been found with AP peaks and modulus, and occasionally, an AP peak with stress. The correlation says that the greater the quantity of AP the higher the modulus, and this, of course, is not possible becuase the quantity of AP cannot change because of aging at a given temperature. This illusion arises because propellant binder has hardened during aging (an increase in modulus) and consequently the binder does not flow as easily under pressure when the ATR unit is assembled. AP at the sample surface is pressed against the surface of the IRE but the binder does not flow as readily when its modulus has increased and, therefore, less binder is present at the IRE surface giving the appearance of an increased quantity of ammonium perchlorate.

The reasoning presented above concerning binder modulus also accounts for an apparent slight decrease in the amount of plasticizer as propellant ages. With less quantity of binder pressed against the IRE, there is an apparent decrease in the quantity of plasticizer in the propellant.

Because of these problems concerning AP and DOA, multiple correlations that involve the AP and DOA peaks are totally invalid even though other peaks involved in the correlation are perfectly legitimate ones.

We manuevered around these problems by not using the statistical analysis routine in E-490 when a spectrum of whole propellant was involved. Instead we used a separate statistical analysis where the peak heights were taken from the IR data reduction routine and manually entered into a statistical analysis program along with mechanical properties.

Where the spectra of AP-leached propellant or the spectra of a sol fraction of propellant were used, of course this problem concerning DOA and ammonium perchlorate did not exist. Thus, the present programming for the infrared data analysis and statistical analysis is not entirely adequate for all possible cases.

Physical Properties Master Tape Reading

At this point in program E-490, the computer accesses the physical properties master tape which was generated using the program E-410. Mechanical properties of the propellant are associated with each of the spectral files by a record number for the mechanical properties. As an example, spectral file 17 may require mechanical properties that are record number 5

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in E-410. This cross-reference between mechanical properties and FTS-10 spectra is made at the time the user instructs the computer for making a given run.

Statistical Analysis

A Thiokol/Huntsville Division statistical analysis program (E-023) was merged with the infrared data reduction program (E-490). The statistical part of the E-490 program is a user option so that the infrared data reduction can be accomplished without using the statistical analysis of the propellant mechanical properties and propellant infrared spectral information.

Three user inputs are required to have the computer perform the statistical analysis. These user inputs identify to the computer the tape file of the mechanical properties that are to be correlated with the spectral information, identify which set of properties is associated with a given spectrum, and finally which of the propellant properties are to be included in the correlation.

Correlations performed by this program are the simple linear regressions and multiple linear regressions. For the simple linear regressions, the computer calculates a correlation coefficient with all input variables to the program such that all peaks and all mechanical properties are correlated against each other. When this portion of the computer operation is finished, it then proceeds to the multiple linear correlations whereby multiple peaks are correlated against mechanical properties and an equation representing the mechanical properties as a function of two or more peak heights is generated. A correlation coefficient is calculated for this relationship along with the standard error associated with each coefficient and the standard error of the estimate provided by the equation. Finally, the computer using the equation computes the predicted mechanical property and then compares it to the actual property and prints both of these values along with the deviation between the actual and the predicted property.

Since not all correlations between infrared peak height changes and mechanical property changes may be pure linear functions, a non-linear regression routine was included in the statistical analysis. The routine selected to examine non-linear correlations involved an exponential function of the independent variables in the analysis; the independent variables being the infrared peak heights. Using the independent variables identified in the multiple linear correlation, the computer squares each of the terms and employs these to establish a non-linear relationship between a propellant mechanical property and peak height changes. Using these new values (selected peak height plus the peak height squared) it then proceeds through the routine formerly used for computation of the multiple linear regressions, but with the squared term it now computes a multiple non-linear regression. When the equations have been established, the computer calculates the predicted mechanical property, compares it with the actual mechanical property, shows the deviation and computes the correlation coefficient for the particular relationship. It then compares the multiple linear correlation with the multiple non-linear correlation and informs the user of which furnishes the best correlation.

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<u>Guide to Using E-490</u>

Computer program E-490 was written for input from cards or a remote terminal. It does, however, require that the FTS-10 spectral tape and the mechanical properties master tape be at the computer location. Table 6 is a form generated during the course of the program to simplify running the program and to assure that all user inputs to the program were properly entered. Following is a brief description of each of the inputs and reference is made to the input number and line item shown in Table 6.

Input 1 is an identification of the charge code or cost center that will pay for the computer's time.

Input 2 is the run time expected for the particular run being submitted. The time is expressed in actual seconds.

Input 3 is an identification number for the FTS-10 magnetic tape containing the spectral information.

Input 4 is the same as input 3 but is entered on a different line.

Input 5 is the designation of the tampe number on which the mechanical property data are stored. This instructs the computer operator which tape to mount for the computer to access during the statistical analysis portion of the program.

Input 6 is designated as "ITAPE =" with room for a two-digit number which is the identification of the FTS-10 spectral tape.

Input 7, "ITOTAL =" is the total number of spectral files that are to be examined during the computer run.

Input 8, "INFILE =" is the FTS data tape file number. A maximum of 50 FTS data files may be treated in any single computer run. The FTS file numbers must be entered in numerical order, beginning with the lowest number and proceeding to the highest number.

Input 9, "MULTPK =" is the number of multiple peak cases that are to be considered by the computer in the run. This is an identification to the computer of the number of spectrum regions that are to be treated with a common baseline. The maximum number that can appear here is six.

Input 10, "NPHOTO =" is the file FTS file number of the best "picture" of each of the multiple peak cases. Here there must be one entry for each of the multiple peak cases considered in input 9.

TABLE 6
USER INPUT TO
IR DATA REDUCTION PROGRAM (E490)

JOB NO. _____

Line	Input Number		
100	1	,___ ___ ___ ___ ___ ___,	Sequence No.
110	2	TIME = _____,	Run Time, Actual Sec.
110	3	___ . _____	User Name
125	4	_____	ID Mech. Prop. Tape
	5	___ ___ ___ ___ ___ ___,	Designation of Tape No. and stored MP data.
250	6	ITAPE = 'TP ___ ___'	Spectral Tape No.
260	7	ITOTAL = ___ ___	Total No. of Files
270	8[b]	INFILE = ___,___,___,___,___,___, ___,___,___,___,___,___,___,___, ___,___,___,___,___,___,___,___, ___,___,___,___,___,___,___,___	FTS File No's. (Max. 30)
280	9[a]	MULTPK = ___	No. Mult. Peak Cases (Max. 6)
290	10[a,b]	NPHOTO = ___,___,___,___,___,___	File No. of Best "Picture" of Each Multpk. Case (1/Multpk)
300	11[a,b]	LLIMIT = _____.,_____.,_____., _____.,_____.,_____.	Wave No. Left Side Multpk. (1/multpk Case)
310	12[a,b]	RLIMIT = _____.,_____.,_____., _____.,_____.,_____.	Wave No. Right Side Multpk. (1/multpk Case)
320	13	WAVNOR = _____.	Normalizing WN.
330	14	MPDISK = 0 or 1	0 = no correlation 1 = correlation request
340	15[b,c]	MPRECS = ___,___,___,___,___,___,___,___, ___,___,___,___,___,___,___,___,___,___,___, ___,___,___,___,___,___,___,___,___,___,___	Mechanical Property Record No's. Must correspond 1:1 with INFILE spectrum no's. (Max. 30)

User Input to IR Data
Reduction Program (F49Ø)

Line	Input Number		
350	16[b],[c]	NPHYSP = ___, ___, ___, ___, ___, ___, ___, ___, ___, ___	Number identification of Physical Properties to be correlated. (Max. 10)
360	17	IPLOT ___	Unnormalized Plot Ø = No; 1 = Yes
370	18	NMPLOT ___	Normalized Plot Ø = No; 1 = Yes
380	19	VALID = ___	Enter Decimal Fraction

JOB NO. _____

NOTES: _____

_____

_____

_____

_____

_____

_____

_____

_____

_____

a) if not using multpk. routine, set value = Ø.

b) Use comma after last number.

c) If not using correlation routine, set value = Ø.

Input 11, "LLIMIT =" is the wave number on the left side of the peak for the multiple peak or COBASE treatment. There must be one entry here for each multiple peak case.

Input 12, "RLIMIT =" is the wave number on the right side of the group of peaks that is to be considered in the COBASE routine. Here, again, there must be one entry per multiple case. For inputs 10, 11, and 12, all numbers must correspond, i.e., the NPHOTO value, the LLIMIT value and the RLIMIT value must all be for the samp multiple peak case and all are treated sequentially. Thus, the second NPHOTO value, the second LLIMIT value and the second RLIMIT value are all for the same file.

Input 13, "WAVNOR =" is an identification of the normalizing wave number for the entire set of spectra.

Input 14, "MPDISK =" is an instruction to the computer whether to perform the statistical correlations or not. A value of 0 entered here instructs the computer that correlations are not desired, an entry of the number 1 here instructs the computer to perform the correlations.

Input 15, "MPRECS =" is an identification of the mechanical property record number on the mechanical property tape which describes to the computer which mechanical property records are to be associated with each of the FTS-10 spectra files. These numbers must correspond in numerical order to the INFILE (input 8) so that the computer can associate a set of mechanical property data with a particular infrared spectrum. Here, as in the case of the INFILE, the maximum number of values that can be entered is 30 and this corresponds to the maxinum number of FTS files that can be treated in any one run.

Input 16, "NPHYSP =" is an identification of the physical properties that are to be used in the statistical analysis. In the physical properties master tape generator program (E-410), space is allowed for 10 properties of the propellant. These properties are numbered 1 through 10; thus, if one wishes to have modulus, strain at maximum stress, and maximum stress correlated with changes in the infrared spectra, then one would specify here 1, 3, and 4, because those are the numbers for those three properties of the propellant.

Input 17, "IPLOT =" is a request for the computer to plot the unnormalized spectra. If such plots are desired, enter the number 1; if such plots are not desired, enter the number 0.

Input 18, "NMPLOT =" is an instruction to the computer to plot the normalized spectra. If one wishes to have plots of the normalized spectra, enter the number 1; if such plots are not needed, enter the number 0.

More detail concerning the use of the E-490 program will be found in the "User's Manual".

E-410 Program Development

Format

Program E-410 is a routine that records data on magnetic tape. I a stored on this tape is accessed by the E-490 computer program and used in the statistical correlation of infrared spectral changes with propellant properties changes.

Data is entered into the computer from cards or a remote teminal with the data being entered inthe following order. The age time of the propellant, the temperature at which aging was performed, and the temperature at which the propellant was tested. Following these three entries, there is space for ten properties of the propellant. The first six properties are identified by name in the computer print-out, these being in order: modulus, strain at break, strain at maximum stress, maximum stress, strain energy density and strain endurance. The remaining four properties are unlabeled and can, of course, be any property that the user wishes to enter. The first six properties of the propellant were labeled simply for the convenience of the user, because the computer deals only with numbers, it does not know what the numbers represent and so the user can enter any property at any location in the program, for a maximum of ten properties.

Guide to Using E-410

This program operates in two modes: mode no. 1 is considered the "create" mode and mode no. 2 is for updating the information that has previously been recorded.

The "create" mode is used to establish a new tape of propellant properties. The data is entered in the order described above in a column oriented, card format; i. e. , each value entered has a defined location on a card. Input can be entered from a remote terminal and the program executed from this terminal.

The format is set so that a record describes the information for the propellant at a given age time, age temperature, and test temperature. When all data has been entered for these conditions, the next line of data is entered and it becomes record number 2. Again, it is the mechanical properties of the propellant at a particular aging time, age temperature and test temperature so that each record can be associated with a particular spectrum of the propellant at those aging conditions.

In the "update" mode, the computer will change, add to or delete information previsosly recorded in the "create" mode. Since in the create mode the computer program ends with the production of a printed tabulation of the data, the user has an opportunity to review the tabulation and to assure himself that the data entered are the correct data. If he finds an eroor has been made, then he can go to the update mode and change that data by record number. If, as the aging program proceeds, he wishes to add the new data to the old data, then he can do this by using the update mode and add the new information with an instruction "add" given to the computer. If the user wishes to remove a line, or record, he can do so using the update mode with the instruction to the computer to "delete". Specific details on the use of program E-410 are in the "User's Manual". An example of a tabulation of properties furnished by E-410 is given in Table 7.

TABLE 7

PRINTED TABULATION OF PROPELLANT PROPERTIES

FROM PROGRAM E-410

FOURIER TRANSFORM INFRARED SPECTROSCOPY - E410 PHYSICAL PROPERTIES
(AFRPL/PCG - THIOKOL/HUNTSVILLE)

PROPERTIES FOR SOLID PROPELLANT : TP-H8278/L-1895

REC NO.	AGE	-AGE TEMP	TEST TEMP	MODULUS	STRAIN AT BREAK	STRAIN AT MAXIMUM STRESS	MAXIMUM STRESS
	(hK)	(F)	(F)	(PSI)	(%)	(%)	(PSI)
1	0	77	77	796.000	0.257	0.247	195.000
2	2	77	77	912.000	0.226	0.214	175.000
3	2	100	77	1005.000	0.227	0.209	180.000
4	2	145	77	941.000	0.253	0.252	180.000
5	2	165	77	1033.000	0.223	0.216	203.000
6	4	77	77	962.000	0.220	0.205	167.000
7	4	100	77	992.000	0.222	0.206	173.000
8	4	145	77	934.000	0.246	0.221	171.000
9	4	165	77	1043.000	0.253	0.245	222.000
10	8	77	77	859.000	0.234	0.213	149.000
11	8	100	77	925.000	0.219	0.201	162.000
12	8	145	77	1056.000	0.228	0.208	174.000
13	8	165	77	1279.000	0.266	0.255	241.000
14	16	77	77	1034.000	0.209	0.196	159.000
15	16	100	77	853.000	0.199	0.143	160.000
16	16	145	77	1139.000	0.222	0.214	205.000
17	16	165	77	1284.000	0.214	0.211	237.000
18	24	77	77	867.000	0.218	0.205	155.000
19	24	100	77	937.000	0.205	0.199	162.000
20	24	145	77	1423.000	0.215	0.212	226.000
21	24	165	77	1467.000	0.231	0.228	265.000
22	36	77	77	937.000	0.231	0.222	181.000
23	36	100	77	1066.000	0.213	0.206	187.000
24	36	145	77	1429.000	0.264	0.264	264.000
25	36	165	77	1437.000	0.251	0.251	272.000

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Task 2 - IR Data Acquisition

Evaluation of Attenuated Total Reflectance Units

Effect of Assembly Pressure on IR Spectra

One of the many variables to consider in acquiring IR data by ATR for quantitative analysis is the force with which the sample is held against the IRE of the ATR. This is a critical variable for any ATR unit, so that the comments made here for the Barnes Engineering Company fixed angle ATR apply to any ATR unit. Variations in the assembly pressure effect the overall magnitude of a spectrum and for one spectrum to be quantitatively compared to another spectrum both spectra must be within the "quantitative" region of magnitude. A variation in this pressure is achieved by varying the amount of torque on the bolts holding the sample against the ATR prism.

Low cost binder propellants, TP-H8270/Mix W-60 and TP-H8278/Mix W-65, were employed in a series of experiments. A single sample (0.02-inch thick) of each of the two propellants was used. The sample was placed in the ATR unit and the torque on the bolts adjusted to the minimum level which would give a spectrum of reasonable magnitude. In the case of TP-H8270, a low modulus propellant, the initial assembly torque was 4 oz-in. The infrared spectrum of the propellant was taken, the ATR unit removed from the spectrophotometer, the torque on the bolts increased to 8 oz-in and the spectrum rerun. In subsequent tests, the assembly torque was increased to 12, 16, 24, and 32 oz-in.

With propellant TP-H8278, the initial torque was 8 oz-in and it was subsequently increased to 16, 24, 32, 40, and 48 oz-in with an IR spectrum of the propellant made at each of the torque levels. The several spectra for each of the two propellants were recorded on magnetic tape and the recorded data reduced by computer.

First interest in these experiments was the relative amplitudes of the very strong ammonium perchlorate peak (1050 cm^{-1}) and the most prominent organic binder peak occurring at 2921 cm^{-1}. The heights of these two peaks were plotted as functions of torque on the assembly bolts. Figure 5 is a plot of the response of TP-H8270 spectral amplitude to assembly pressure. This is a low-modulus propellant, so the torque on the assembly bolts did not exceed 32 oz-in. Notice that the amplitude of the peak at 1050 cm^{-1} grows at a considerably higher rate than the organic peak at 2921 cm^{-1}. Notice also that the 2921 peak is plotted two ways; first, a plot of just the maximum amplitude of that particular peak and second, a plot of peak height; i.e., the maximum amplitude minus the baseline amplitude. This latter plot is before normalizing; obviously, after normalizing, that peak height remains the same under all conditions. Plotting the peak height shows that there is less change when one subtracts the influence of baseline variation from the
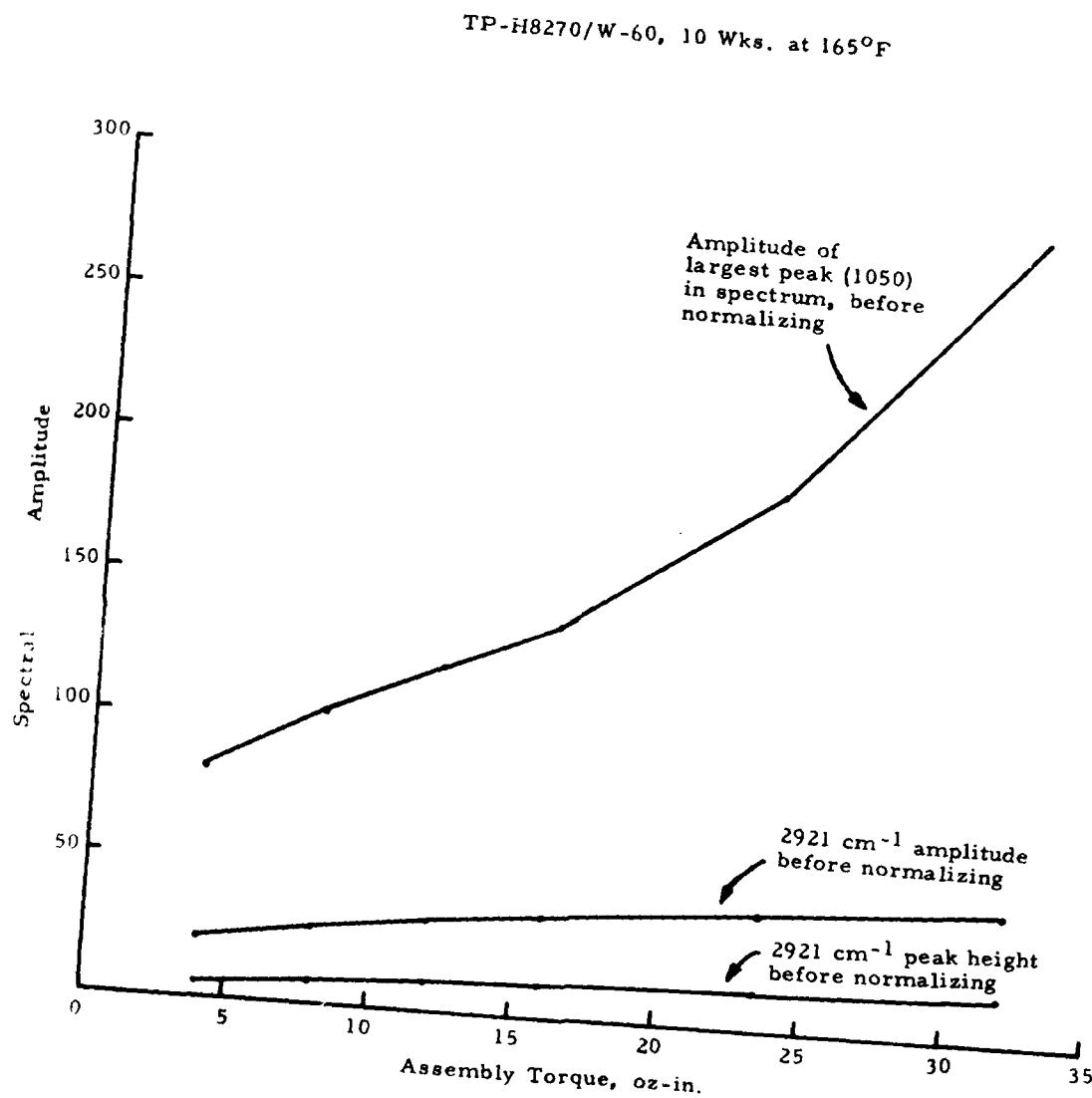
Figure 5.   Effect of Assembly Pressure On Spectral Amplitude
of Propellant TP-H8270 (Low Modulus)

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peak amplitude. This says that some of the variation due to assembly torque will be removed simply by subtracting baseline amplitude from peak amplitude.

The higher modulus propellant, TP-H8278, is plotted on Figure 6. Final torque on the assembly bolts was 48 oz-in to achieve an overall maximum amplitude at 1050 cm^{-1} of near 160. This same amplitude on the lower modulus propellant, TP-H8270, was reached at a torque value between 16 and 24 oz-in. Notice on Figure 6 the response of the 2921 cm^{-1} peak and particularly the fact that is has a higher slope than the corresponding plot for the Figure 5 propellant. This tells us that high modulus propellants will require higher assembly torque (an obvious conclusion) but also that assembly torque has more influence on the magnitude of the critical organic peaks. In both plots notice that the response of the spectral amplitude to assembly torque is not linear over the entire range of assembly torques investigated. Instead, in each case there is a region where the maximum absorbance value responds linearly to assembly torque. This occurs for the 1050 cm^{-1} peak near an absorbance value of 100. In both cases, the response of the organic peak at 2921 was linear in the same region.

The response of the specific peaks, within each spectrum, to assembly torque is given in Figures 7 and 8 for TP-H8270 and TP-H8278, respectively. Data plotted here are normalized. Note on each plot that there are two vertical axes; the upper one is at a scale ten times the lower one, so that even though the variation of peak height with assembly torque in the lower set of plots appears large, the change is actually quite small and, in most cases, is less than one absorbance unit.

In reference to Figure 7, the following comments are made concerning the effects of assembly torque. First of all, the vast majority of the small organic peaks have a response that is similar to each other. In the area where the overall spectral amplitude is in the vicinity of 100 absorption units; i.e., a torque level of 8 to 16 oz-in, all of the peaks exhibit very little change in their height. This comment is made with particular reference to those peaks plotted at the bottom of the Figure where the relative peak height scale is expanded. Looking now at the upper part of that plot, where the relative peak height scale is contracted, indicating that the amplitude change will be large, one finds that the plot of the 1738 peak is particularly flat in this assembly torque region and that the peak at 911 is also relatively flat in this region, while the peak at 965 shows a great deal of change with assembly torque. This says that the peak at 965 is probably very unreliable as an indicator of change in the organic binder. We have found this to be true when we try to correlate the peak changes at 965 cm^{-1} with propellant mechanical property changes. This apparently almost random behavior of the peak at 965 is due to the fact that it, in whole propellant, rides on the side of the large AP peak located at 1050 cm^{-1} and for some reason responds

44
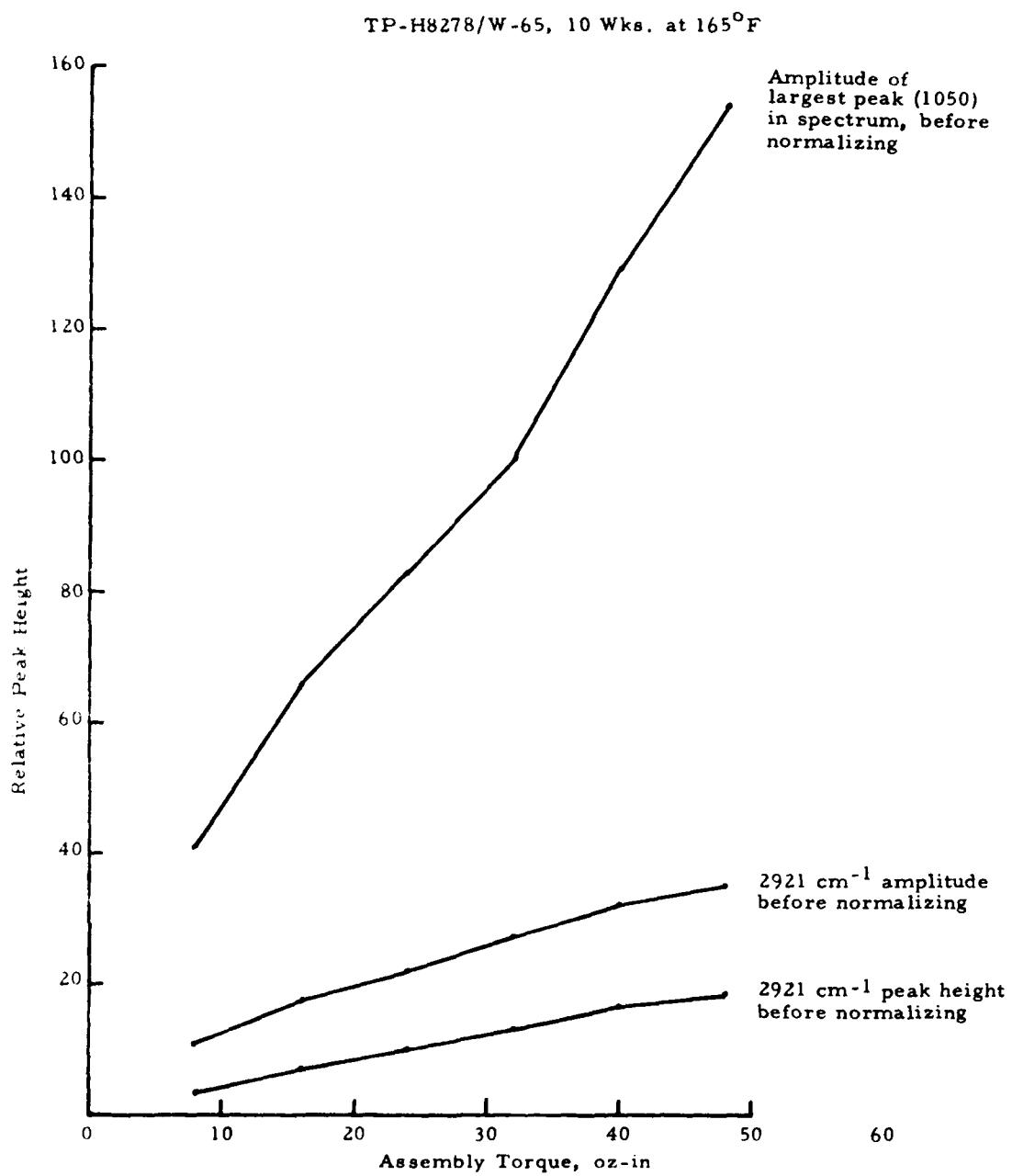
Figure 6. Effect of Assembly Pressure On Spectral Amplitude.
of Propellant TP-H8278 (High Modulus)

45
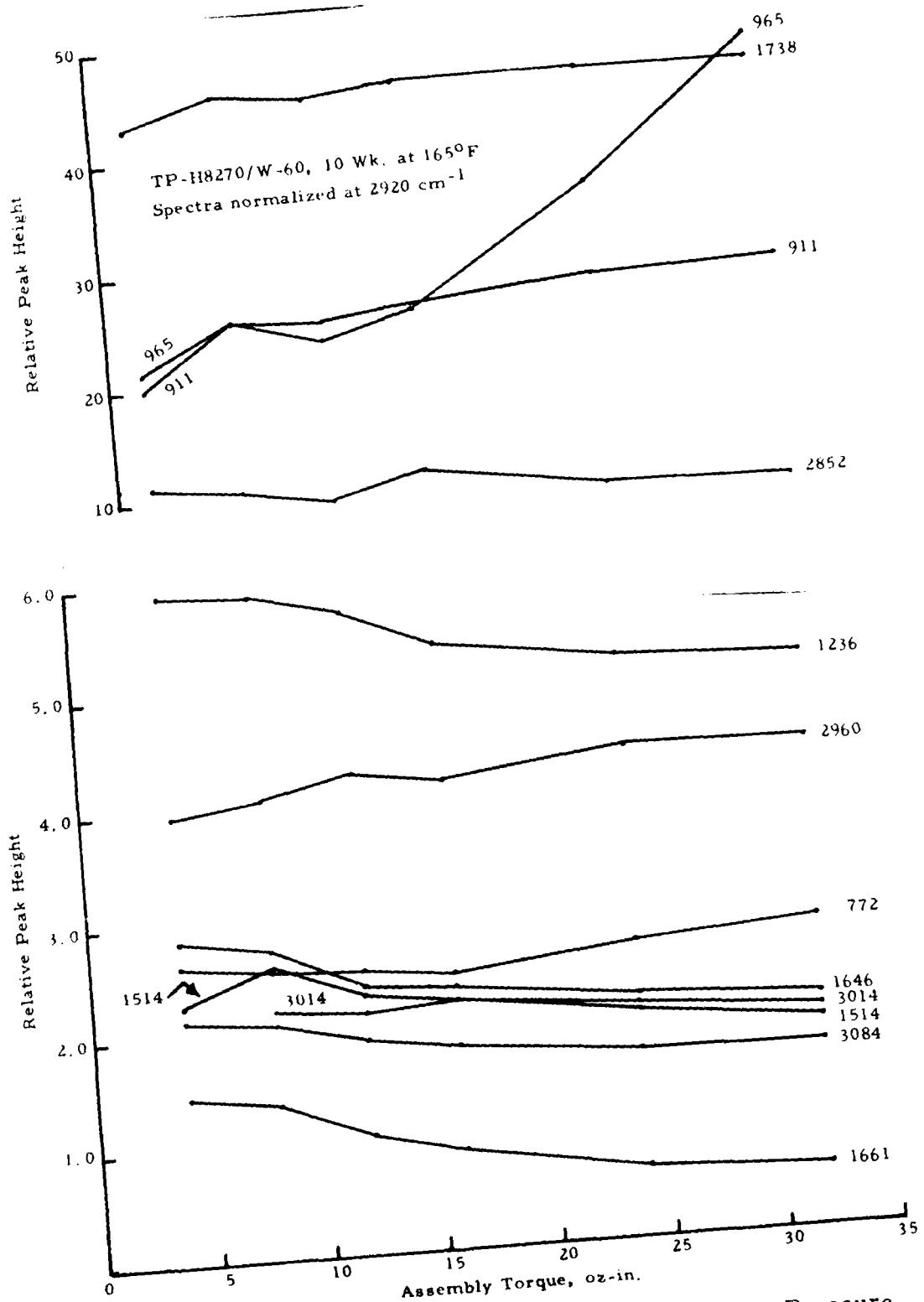
Figure 7. Response of Peak Height to ATR Unit Assembly Pressure
(Torque on Assembly Bolts)

46
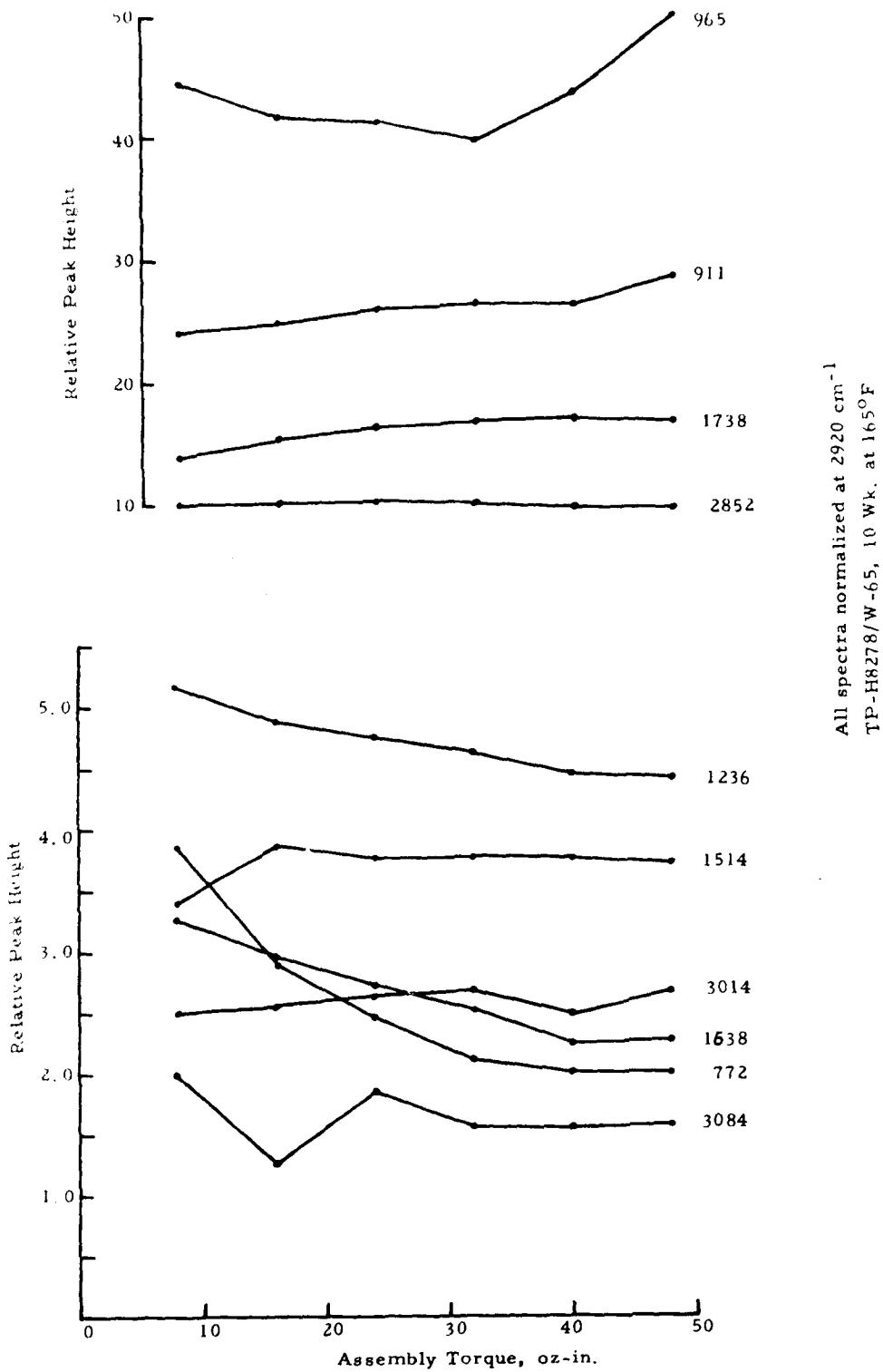
Figure 8.   Response of Peak Height to ATR Unit Assembly Pressure
(Torque on Assembly Bolts)

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to changes in the height of that AP peak to a greater extent than does the peak located at 911. The peak at 911 cm^{-1} is located on the lower portion of the large AP peak at 1050 cm^{-1}.

Information plotted on Figure 6 reveals much the same trends as was observed in the Figure 7 plots. If one looks in the region of near-linear response, 16 to 32 oz-in torque, as determined from Figure 6, one finds that in the lower graph on that Figure the organic peaks follow the same general trend and are roughly parallel to one another with only very small changes in the height of the peaks. The peak at 772 shows the greatest change, probably because it is influenced by the strong ammonium perchlorate absorption near 650 cm^{-1}. The peak located at 1236 cm^{-1} shows some change which may be due to the proximity of two strong ammonium perchlorate absorptions at 1420 and 1050 cm^{-1}. Location of the baseline for this peak is affected by the magnitudes to those two AP peaks. Looking now at the set of plots at the upper portion of Figure 8, we find again that the 965 peak undergoes some very drastic changes in response to assembly torque; although, in the selected region of assembly torque (16 to 32 oz-in) this particular peak is at its most linear showing the least response to assembly torque. Comments concerning this peak and the large AP absorption at 1050 cm^{-1} made for the Figure 7 plots are equally true here. Notice also that the 910 cm^{-1} peak responds least in the selected assembly torque region.

Major conclusions that can be drawn concerning the effects of assembly pressure are as follows:

Keeping the maximum absorption in any spectrum of whole propellant in the region of 80 to 120 or perhaps 130 absorption units provides information which will still be quantitatively usable. So, this more complete and precise analysis of the effect of assembly torque on the linearity of response of spectral peaks has not changed our opinion on how the spectral information should be acquired. The correlation of the heights of several peaks to changes in propellant mechanical properties must be highly suspect because of their inherent variation due to association with ammonium perchlorate. Peaks to be careful of are those occurring at 772 cm^{-1} and 965 cm^{-1}. We can also expect some data scatter in trying to correlate spectral changes with mechanical property changes, simply because we now see that there is a small response of the propellant peak height to the pressure used in holding the sample against the ATR prism.

Where the IR spectrum of AP-leached propellant, AP-leached gel fraction or propellant sol fraction is made, the general rules of quantitative IR spectroscopy apply. The rules dictate that the most quantitative amplitude region lies below 100 absorptive units and above 20 units. Therefore, the maximum amplitude of a spectrum should lie between 50 and 100 units.

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Barnes Engineering Unit

The Barnes Engineering Company unit employed throughout the project is a non-beam condensing ATR with a fix angle (45°) and was used with a KRS-5 IRE. In order to make best use of IR data accumulated in the early parts of the FTIS project and data collected even before the project started, all of the data reported (except that designated as being accumulated with the Harrick Scientific unit) were measured using the Barnes unit. That unit became the "standard" simply because the vast majority of the data were measured using it. This does not in any way imply that the Harrick unit is unsatisfactory or un-usable, only that it was not employed because it was not available for testing early enough in the program to be used. One of the very important facts discovered when the Harrick unit was evaluated was that the same ATR and IRE must be used throughout an aging program in order to have the spectra quantitatively comparable.

Following are some discussions concerning the Barnes ATR unit and the Harrick ATR unit, a comparison of their effects with identical samples of propellant. The fact that the samples are AP-leached is of no significance, the important fact is that all samples were the same so that the comparison is valid.

Samples of TP-H8156 propellant aged at 150°F were washed free of ammonium perchlorate over a period of 23 hours using the technique described in Appendix B. Infrared spectra of the propellant at 1/2, 1, 2, 3, and 6 months aging were run using the Barnes ATR unit with a KRS-5 was used in this series. The torque on the sample holder was adjusted such that the maximum absorption in the spectrum of each sample would be in the order of 100 absorption units. A review of the spectra thus made showed them to be free of ammonium perchlorate absorptions. The effect of aluminum on the various spectra was electronically subtracted. Figure 9 is the infrared spectrum of the propellant aged for 1/2 month at 150°F with ammonium perchlorate leached out by water and the spectral influence of aluminum subtracted.

The spectral data were hand-reduced, and these data are tabulated in Table 8. Correlation of the spectral peak heights with propellant mechanical properties was identified by computing a linear correlation coefficient and these coefficients are also given in Table 8. There were two correlations having magnitudes of greater than 0.8. These occurred with strain and the peaks located at 1510 and 1440 cm^{-1}. A plot of these peak height changes versus time is given in Figure 10.
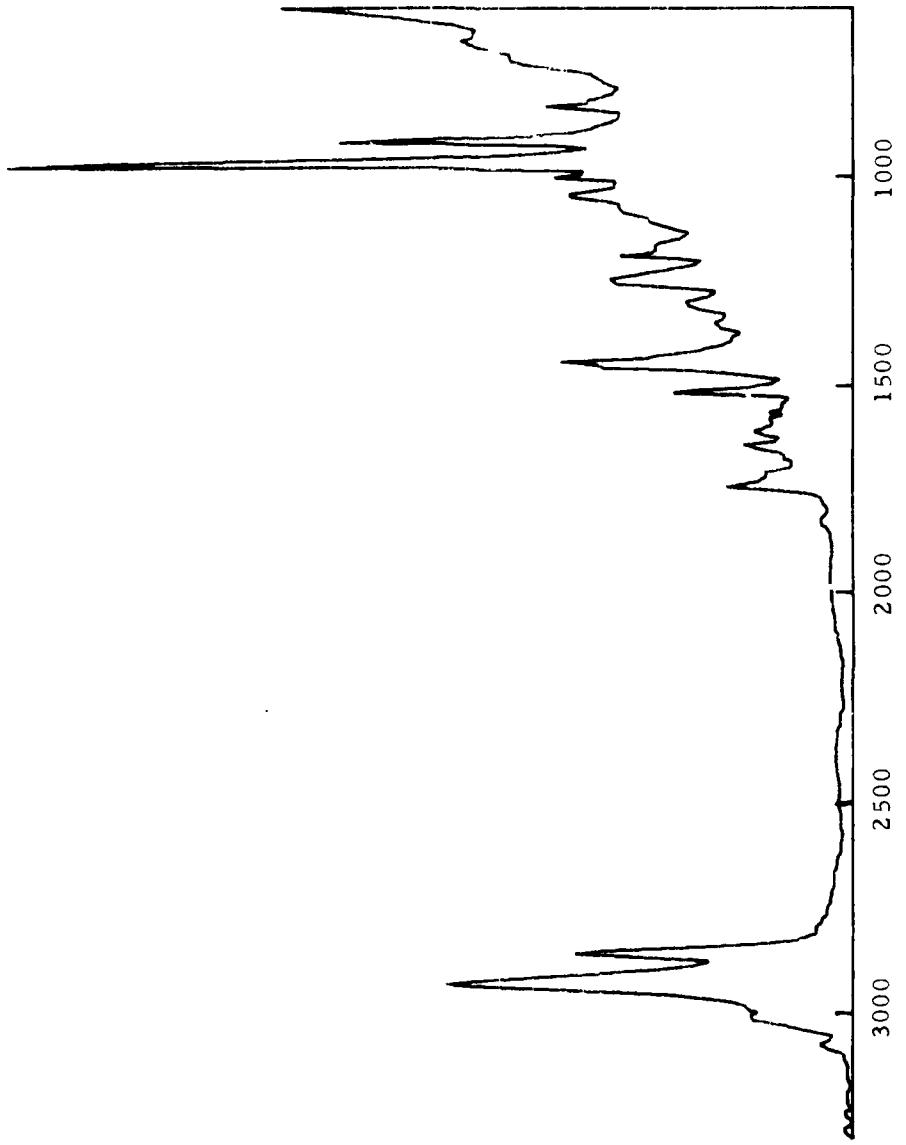
Figure 2. Spectrum of TP-H8156 Aged 0.5 Month at 150°F: AP Leached Al Subtracted. Made with Barnes ATR and KRS-5.

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TABLE 8

DATA CORRELATIONS - SPECTRAL PEAK HEIGHTS FOR TP-H8156
AGED 6 MONTHS AT 150°F WITH MECHANICAL PROPERTIES

Wave No., cm^{-1}	Aging Time, Months						Correlation Coefficients		
	Φ Mo.	.5 Mo.	1 Mo.	2 Mo.	3 Mo.	6 Mo.	E	σ	ε
3080	5.4	5.6	5.5	5.9	5.7	5.4	Δ <1 mm		
2920	87.6	87.6	87.6	87.6	87.6	87.6	Normalizing Peak		
2850	53.6	52.6	51.3	52.0	52.7	51.3	.0003	.1844	.5034
1740	25.4	26.2	25.0	25.9	25.8	25.4	-.1646	-.3963	-.3503
1710	12.3	10.0	15.3	9.0	9.0	12.3	-.0192	.2263	.4956
1640	9.5	11.1	9.8	9.4	9.4	9.5	-.4352	-.4845	.1905
1610	7.9	6.7	7.8	7.5	7.7	8.6	.7551	.7749	-.2540
1510	34.1	35.0	35.7	36.1	36.4	36.3	.1227	-.2075	-.8328
1440	63.9	62.0	62.2	60.9	60.1	61.0	-.0785	.2986	.8680
1350	5.7	5.5	5.9	5.4	5.3	5.8	Δ <1 mm		
1300	10.0	11.1	11.1	11.2	11.3	11.1	Insufficient Δ last 5 No's.		
1250	29.2	30.6	30.9	31.0	30.4	31.0	-.1636	-.4660	-.6888
1190	19.7	23.8	22.3	24.1	23.9	22.5	-.3396	-.6958	-.6821
1170	8.1	12.3	10.5	12.3	12.3	11.1			
1040	14.9	14.7	14.4	15.1	15.2	14.1			
965	163.3	179.1	178.6	180.0	174.6	177.8	-.3323	-.6368	-.6134
910	73.7	78.7	79.2	79.3	77.9	79.7	-.1562	-.4762	-.7003
825	24.6	22.8	22.3	23.2	23.5	22.1	.0308	.2676	.5150
Norm. factor	1.0355	1.0367	1.0367	1.0318	1.0000	1.0186			

NOTES:

1) Spectra run in Barnes apparatus w/KRS-5 IRE at 45° angle and torque to provide near 100 absorption units.

2) Aluminum spectrum subtracted.

3) AP leached w/H$_2$O at 35°-40°C for 23 hours.

TP-H8156 Aged 6 Mo. at 150°F, AP leached w/H₂O.
Spectra run w/Barnes apparatus, KRS-5 IRE, 45°
Correlation coefficients ≥ ± 0.8
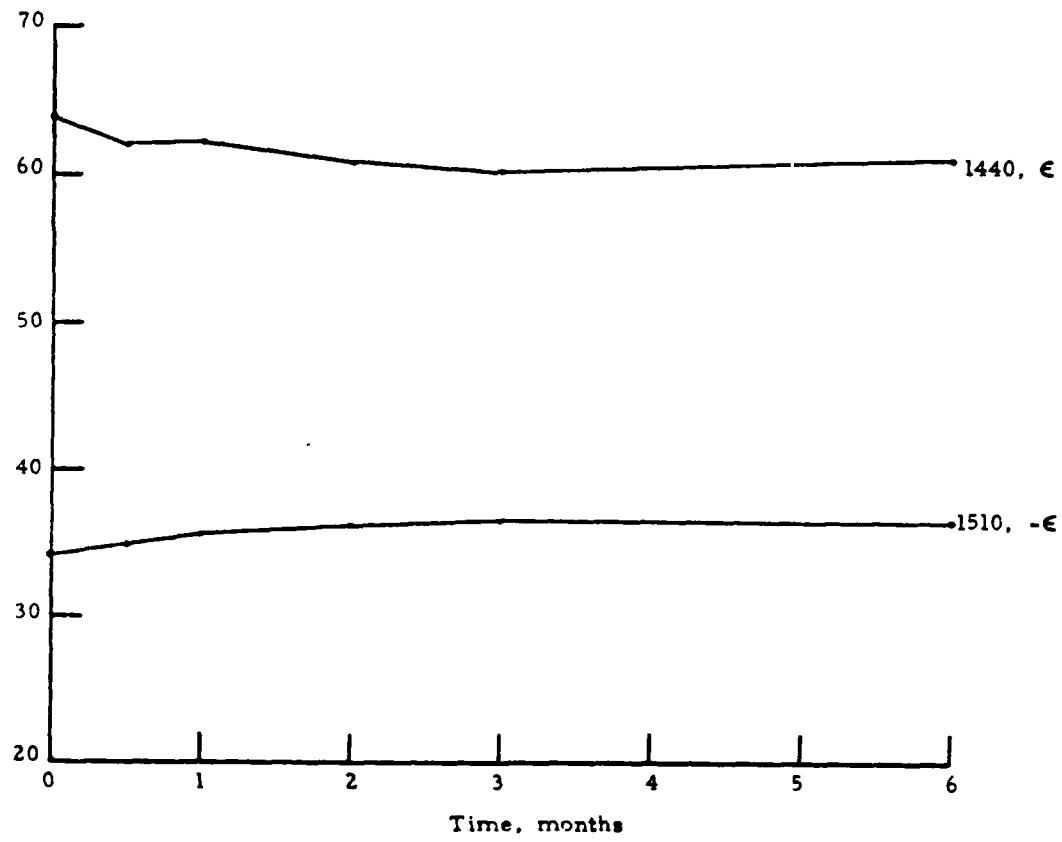
Figure 10. Peak Height Changes vs Time for TP-H8156 Aged 6 Months at 150°F

1) Harrick ATR Germanium IRE

A second set of TP-H8156 propellant samples aged at 150°F was washed for 21 hours according to the procedures described in Appendix B. Half of each propellant sample was used for the spectra presented and described here; the remaining half of each propellant sample was used for evaluation of the Harrick ATR unit with an Irtran-4 IRE.

Infrared spectra of these propellant samples were taken using a germanium internal reflection element at an indicated angle of 60°. Previous evaluation of this apparatus (this evaluation will be described in Task 2) indicated that approximately 40 oz-in of torque would be required to furnish a spectrum of reasonable magnitude. This value was a constant for all of the spectra. By reviewing the minimum (MNY) and maximum (MXY) values listed on the title block (upper left) of each spectrum, it can be seen that the magnitude of each spectrum was approximately the same. These spectra are displayed on Figures 11-16.

Use of a germanium IRE appears to provide at least one advantage; the baseline drift below 2000 cm^{-1} is considerably less than the baseline drift created with a KRS-5 IRE. Spectra shown in Figures 11-16 have not had aluminum subtracted from them and the baseline drift in these spectra is slightly less than the baseline drift found with the KRS-5 spectra, even after the effect of aluminum has been subtracted.

There is another difference in the quality of the spectra from the germanium IRE compared with the spectra using KRS-5. In the case of germanium, the peak heights below 2000 cm^{-1} generally are smaller than with the KRS-5. Also, the height of the peaks in the CH$_x$ region, i.e., 2800 to 3100 cm^{-1}, are slightly smaller in the germanium IRE. This reduces somewhat the accuracy with which the peak heights may be measured using the current technique, i.e., measuring the peaks with a vernier caliper. When the computer program is finished, the determination of peak heights will be of equal accuracy whether the germanium or the KRS-5 is used, because the spectral information in the computer is in digital form and magnitude of each spectral point is recorded to four decimal places. Based on the information we have now, we feel that the smaller peak heights with the germanium IRE will not be a significant problem.

53
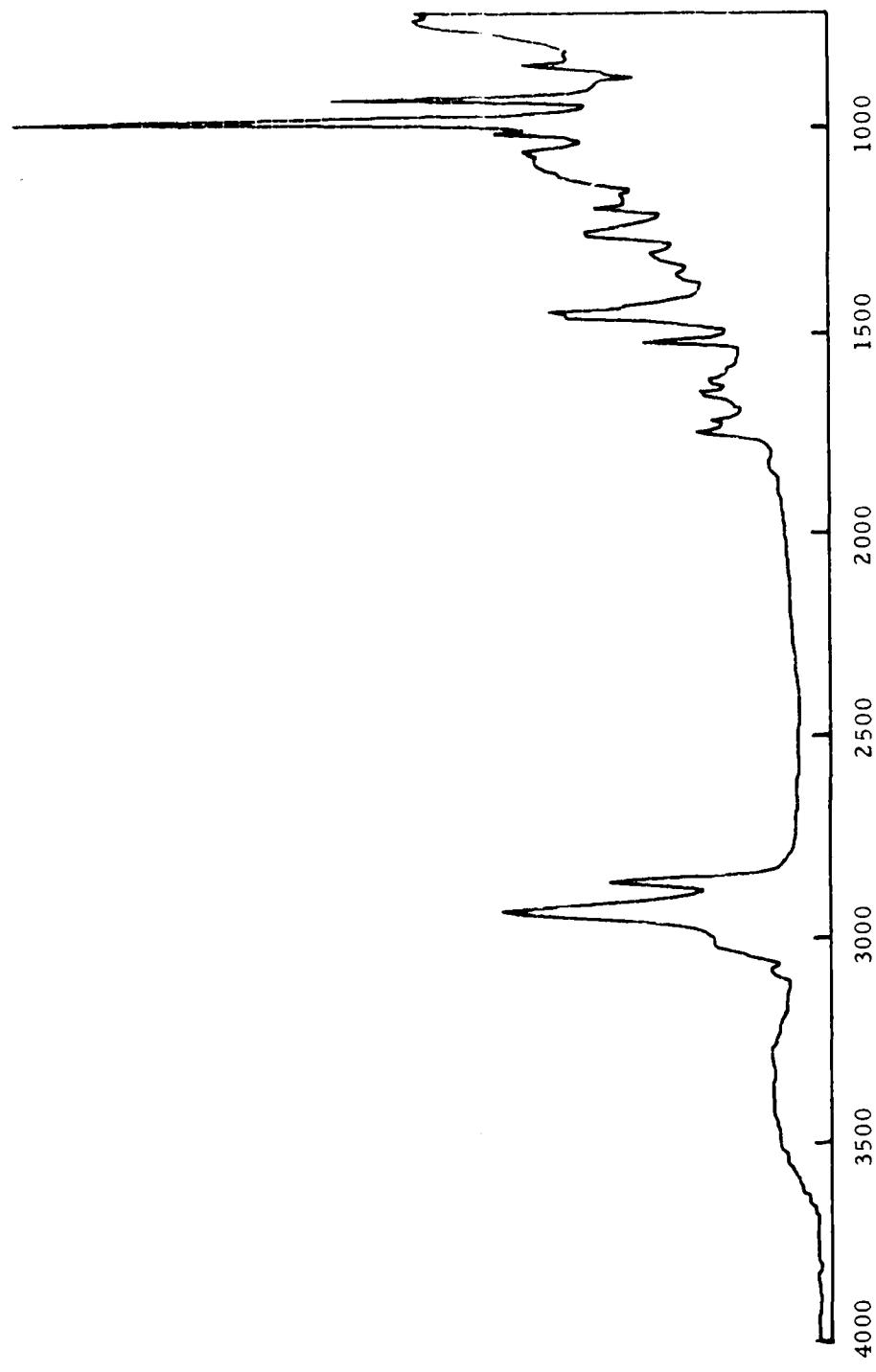
Figure 11. Spectrum of TP-H8156 Aged Zero Time: AP Leached. Made with Harrict ATR and Ge.

54
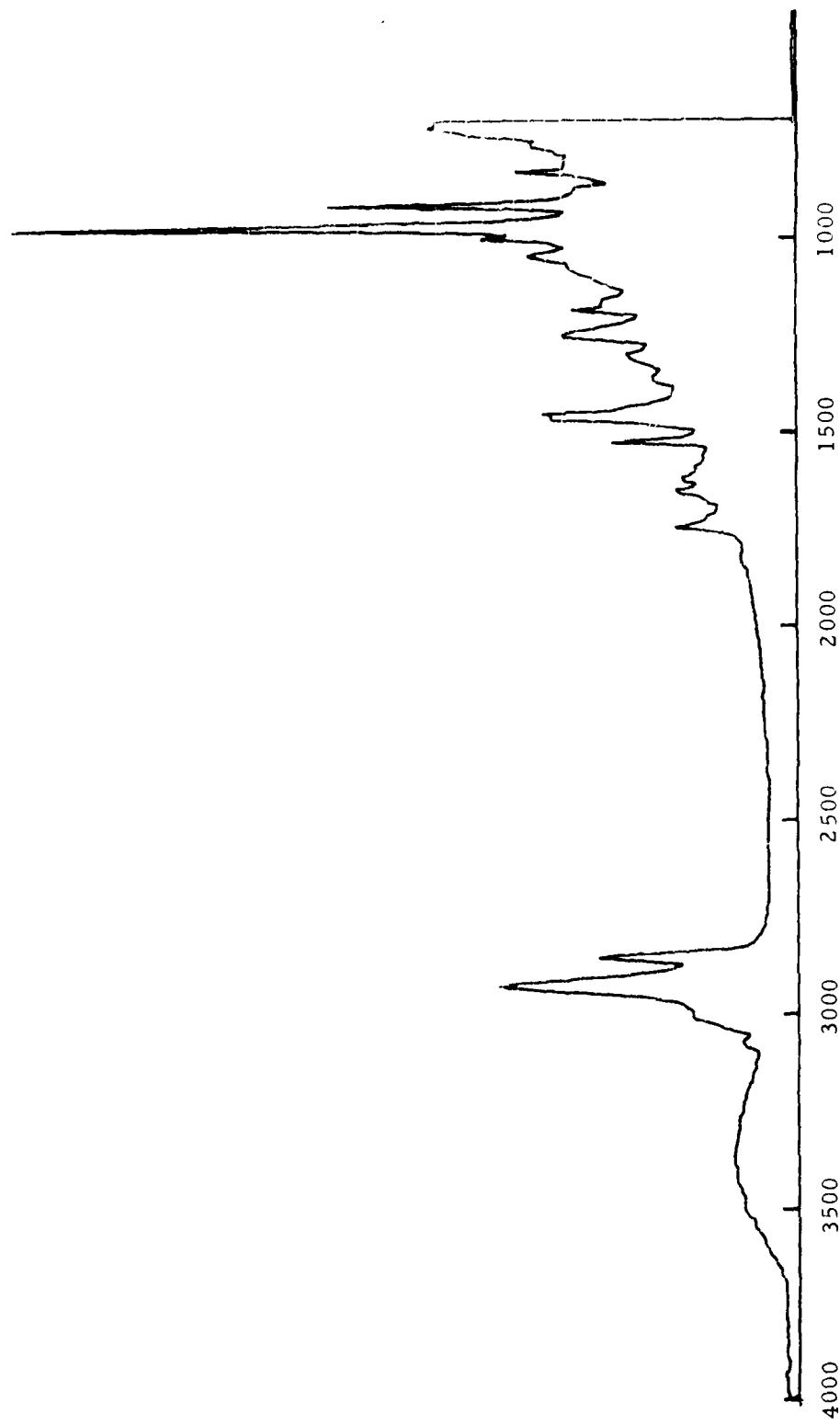
Figure 12. Spectrum of TP-H8156 Aged 0.5 Month at 150°F; AP Leached. Made with Harrick ATR and Ge.

55
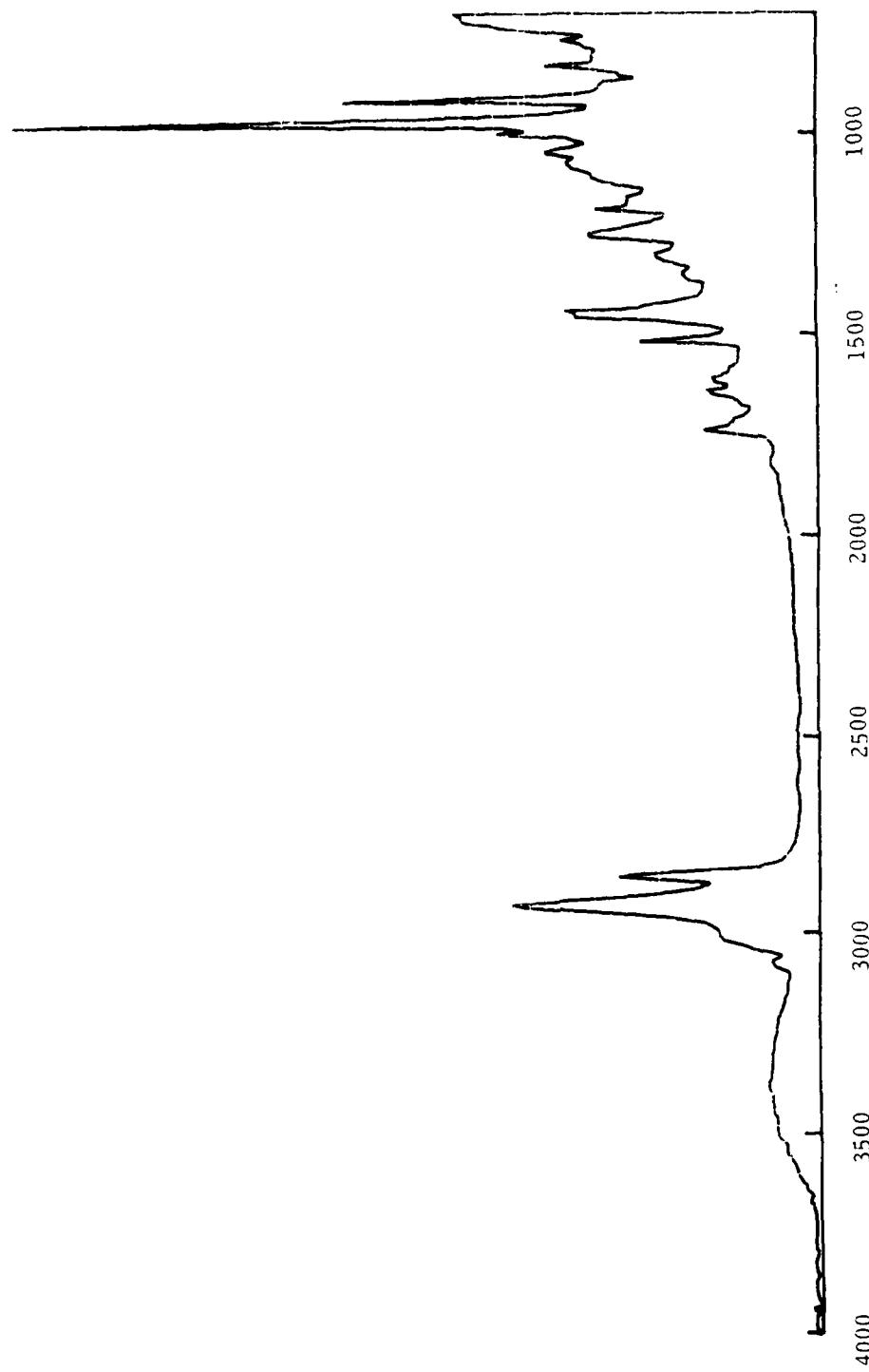
Figure 13. Spectrum of TP-H8156 Aged 1 Month at 150°F; AP Leached.
Made with Harrick ATR and Ge.

56
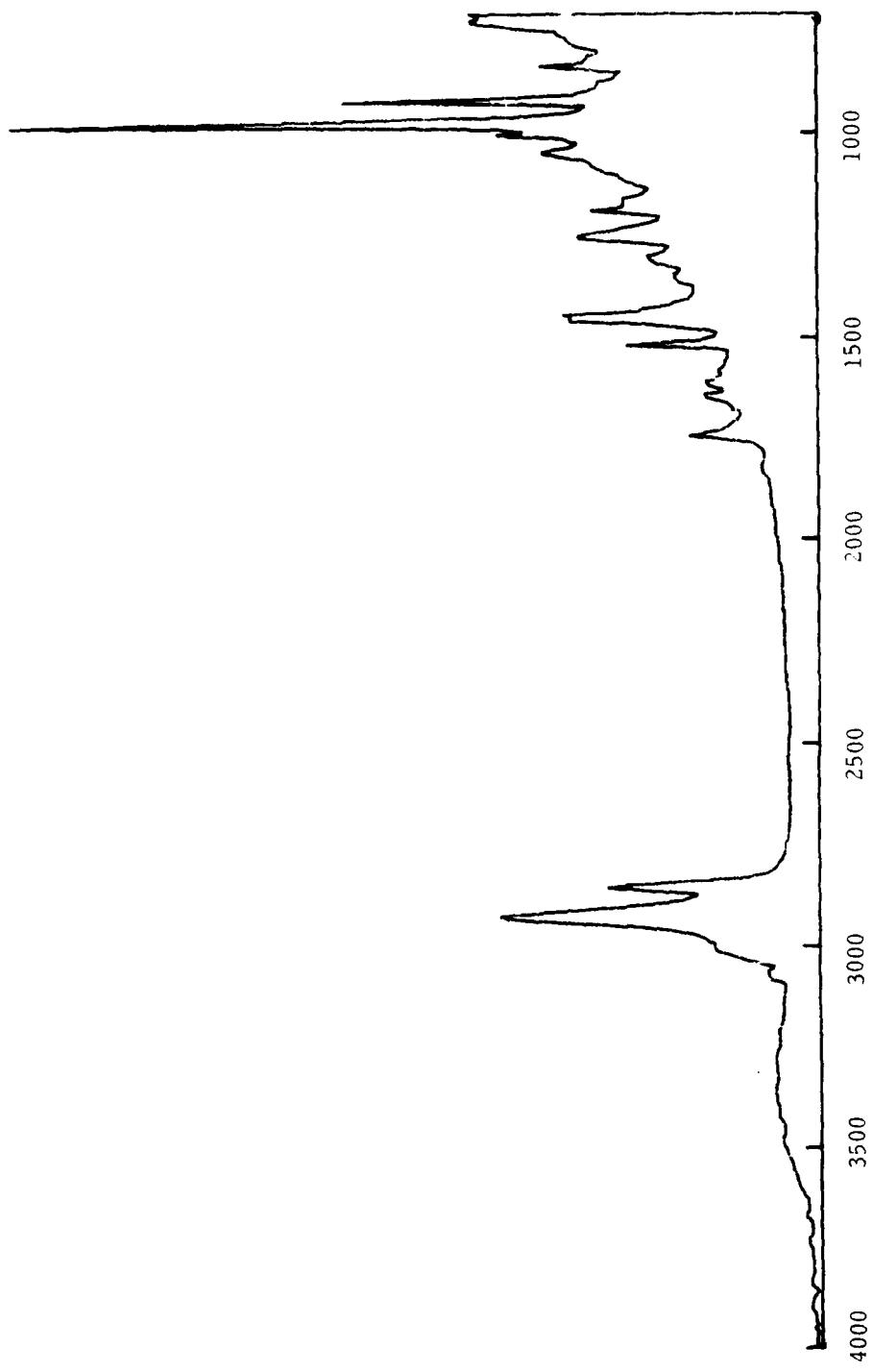
Figure 14. Spectrum of TP-H8156 Aged 2 Months at 150°F; AP Leached/Made with Harrick ATR and Ge.

57
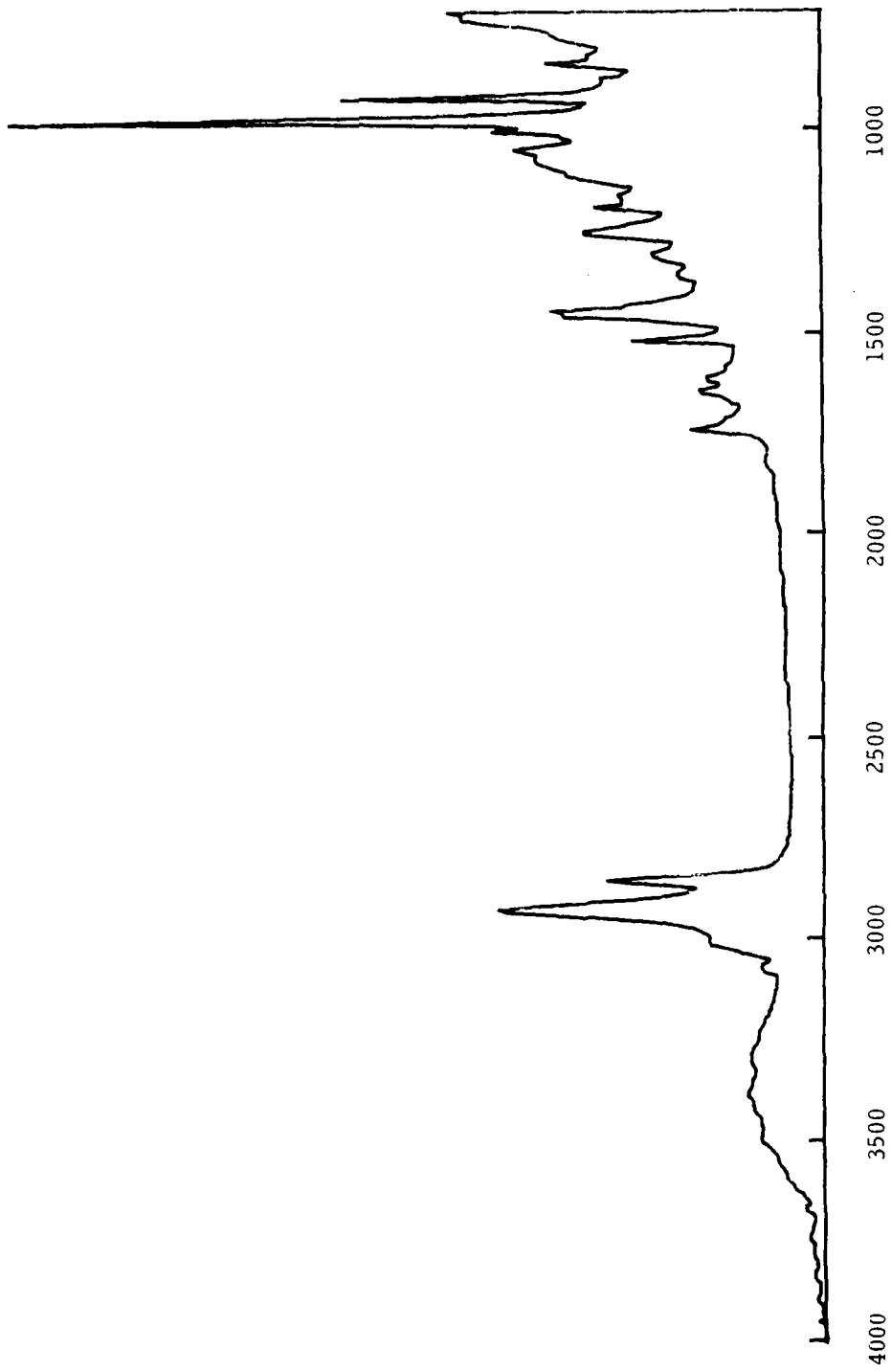
Figure 15. Spectrum of TP-H8156 Aged 3 Months at 150°F; AP Leached. Made with Harrick ATR and Ge.

58
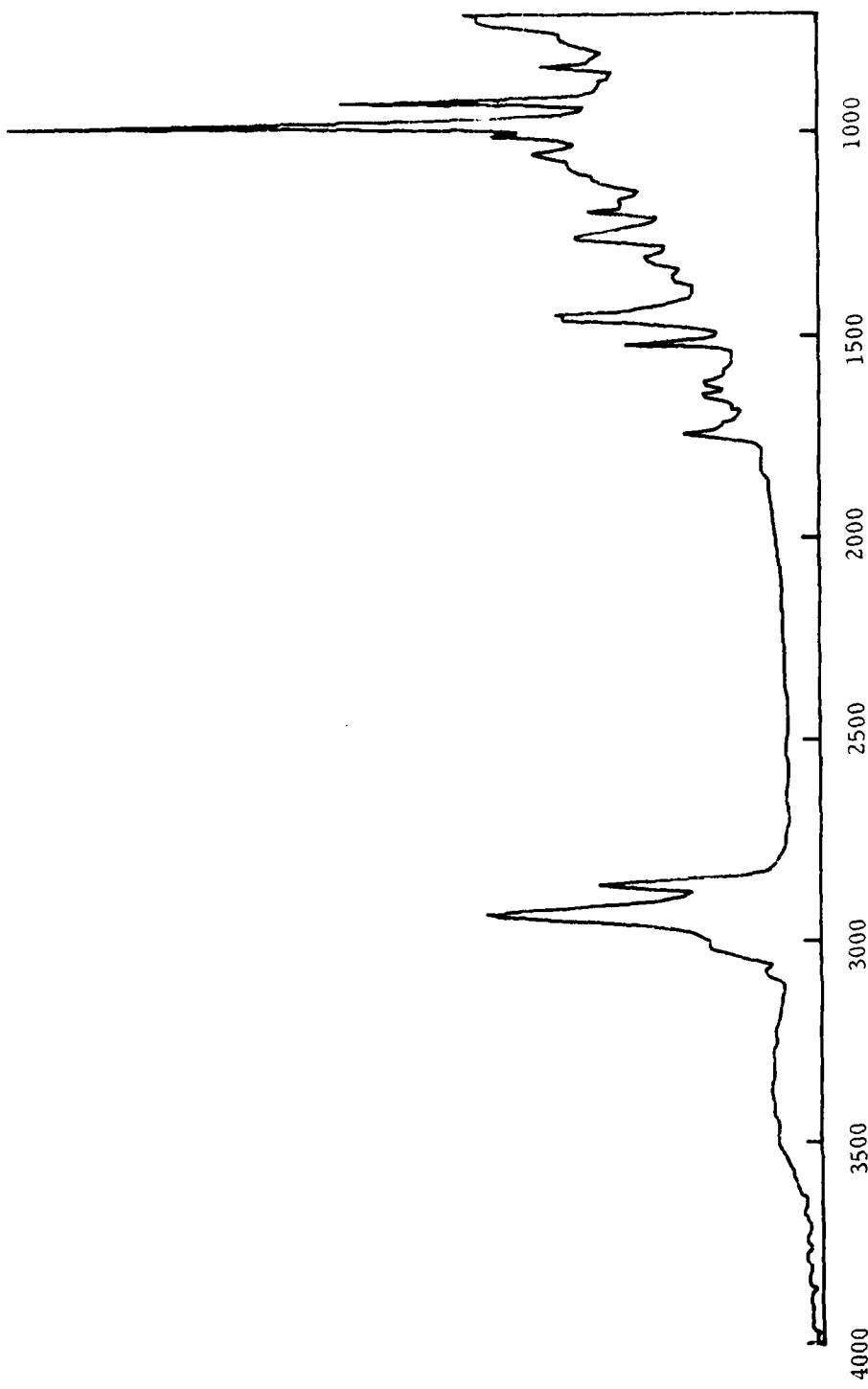
Figure 16.   Spectrum of TP-H8156 Aged 6 Months at 150°F; AP Leached
Made with Harrick ATR and Ge.

59

Spectral data were reduced using the data reduction technique "D" and these reduced and normalized data are reported in Table 9 along with the correlation of these spectral data with propellant mechanical properties.

Here, again, there are no correlation coefficients of a magnitude greater than 0.9, the same phenomenon that was discovered with the KRS-5 data. There are, however, five peaks which correlate with propellant mechanical properties at greater than 0.8. These five peaks have been plotted against time on Figure 17. Although there were no very strong numerical correlations, there are some very strong curve shape correlations. Principally, the peak at 965 cm^{-1} has a strong inverse relationship by curve shape to modulus and stress. This can be seen by comparing the data plotted on Figure 17 with that plotted on Figure 8. There is also a strong curve shape correlation for the peaks at 1250 cm^{-1} and 1740 cm^{-1}; these peaks hold an inverse relationship to strain. Correlations found with the germanium internal reflection element are not the same as those found with KRS-5.

2) Irtran-4 IRE

Infrared spectra of the propellant were made using the Harrick ATR unit with an Irtran-4 (zinc selenide) IRE. All spectra were made at an angle of incidence of 60° with the bolt on the sample holder tightened to a torque of 24 oz-in. One of the most notable features of the spectra made using Irtran-4 is the severe baseline drift... even more severe than that found in spectra made using KRS-5. The height of the peak at 965 cm^{-1}, which in KRS-5 and germanium was the largest peak in the spectrum, is with the Irtran-4 a relatively small peak, while the peak located at 2920 cm^{-1} is by far the largest peak in the spectrum; the converse was true with spectra made using germanium and KRS-5. This very dramatic change in the appearance of the spectrum is caused by the difference in refractive index of the three materials and in the case of the KRS-5 also caused by difference in the angle of incidence of the infrared light. Spectra made using Irtran-4 and germanium were at the same angle of incidence of light (60°), while the KRS-5 spectra were made at an angle of incidence or 45°.

Figure 18 is a sample spectrum made with the Irtran-4. This is the propellant at "0" aging time with the ammonium perchlorate leached out but without having subtracted the spectral influence of aluminum. The general shape of the spectrum on Figure 19 should be compared with Figure 11 made with germanium and with Figure 4 for a spectrum made with KRS-5. All three of these spectra have had the aluminum subtracted and the comparison shows the effect of the IRE on the spectrum's general shape.

Spectra shown in Figures 19-24 are for the "0" through six months aging time at $150^{\circ}F$. Reducing the baseline drift by electronically subtracting the spectral influence of aluminum served primarily to enlarge the spectra and to make the measurement of peak heights considerably more accurate. Comparing these spectra with those made using germanium and KRS-5 shows that with

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TABLE 9

DATA CORRELATIONS - SPECTRAL PEAK HEIGHTS FOR TP-H8156
AGED 6 MONTHS AT 150°F WITH MECHANICAL PROPERTIES

Wave No., cm⁻¹	Aging Time, Months						Correlation Coefficients		
	Φ Mo.	.5 Mo.	1 Mo.	2 Mo.	3 Mo.	6 Mo.	E	σ	ϵ
2920	65.7	65.7	65.7	65.7	65.7	65.7			
2850	39.2	40.0	41.4	40.2	39.5	39.1	-.8331	-.7444	.3117
1740	19.1	19.0	18.4	20.8	19.6	20.6	.5499	.2864	-.8202
1710	11.4	4.7	4.8	4.0	5.2	5.3	.3441	.6701	.4363
1640	8.8	8.4	8.5	7.6	8.6	7.9	-.1615	.0989	.7485
1610	5.5	5.9	6.1	5.9	5.3	6.4	.1952	.0789	-.3563
1510	28.9	32.0	30.7	32.4	30.8	31.9	-.0959	-.4553	-.7803
1440	52.4	49.6	48.9	47.2	50.0	47.6	-.0062	.2915	.7692
1350	5.0	5.1	5.1	4.8	4.5	4.8	.0241	.3978	.8282
1300	8.6	9.0	8.7	8.7	8.4	8.7	-.2934	-.3386	-.0264
1250	25.8	27.5	26.8	28.3	27.2	27.5	-.1204	-.4755	-.8050
1190	17.6	21.2	19.8	21.2	19.3	19.8	-.4190	-.7051	-.5285
965	171.8	180.3	175.9	175.8	171.0	167.8	-.8639	-.8283	.3430
910	81.7	83.5	81.3	81.2	80.6	78.0	-.7756	-.6271	.6095
Norm. factor	1.0170	1.0683	1.0379	1.0186	1.0314	1.0000			

NOTES:

1) Spectra run in Harrick apparatus w/Ge IRE at 60° angle and 40 oz-in torque.

2) Aluminum spectrum not subtracted.

3) AP leached w/H_2O at 35°-40° for 21 hours.

61
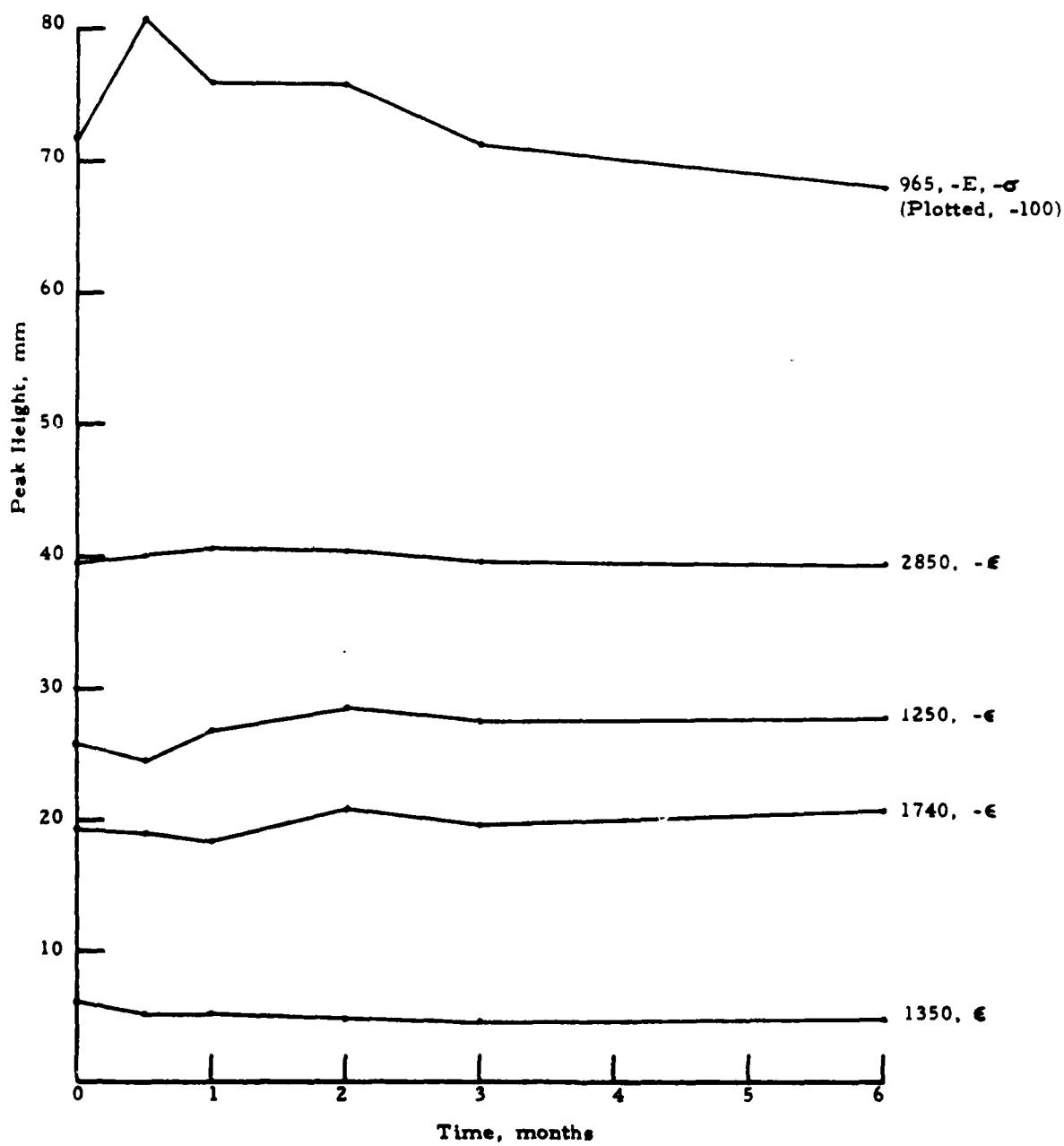
Figure 17. Peak Height Changes vs Time for TP-H8156 Aged 6 Months at 150°F

62
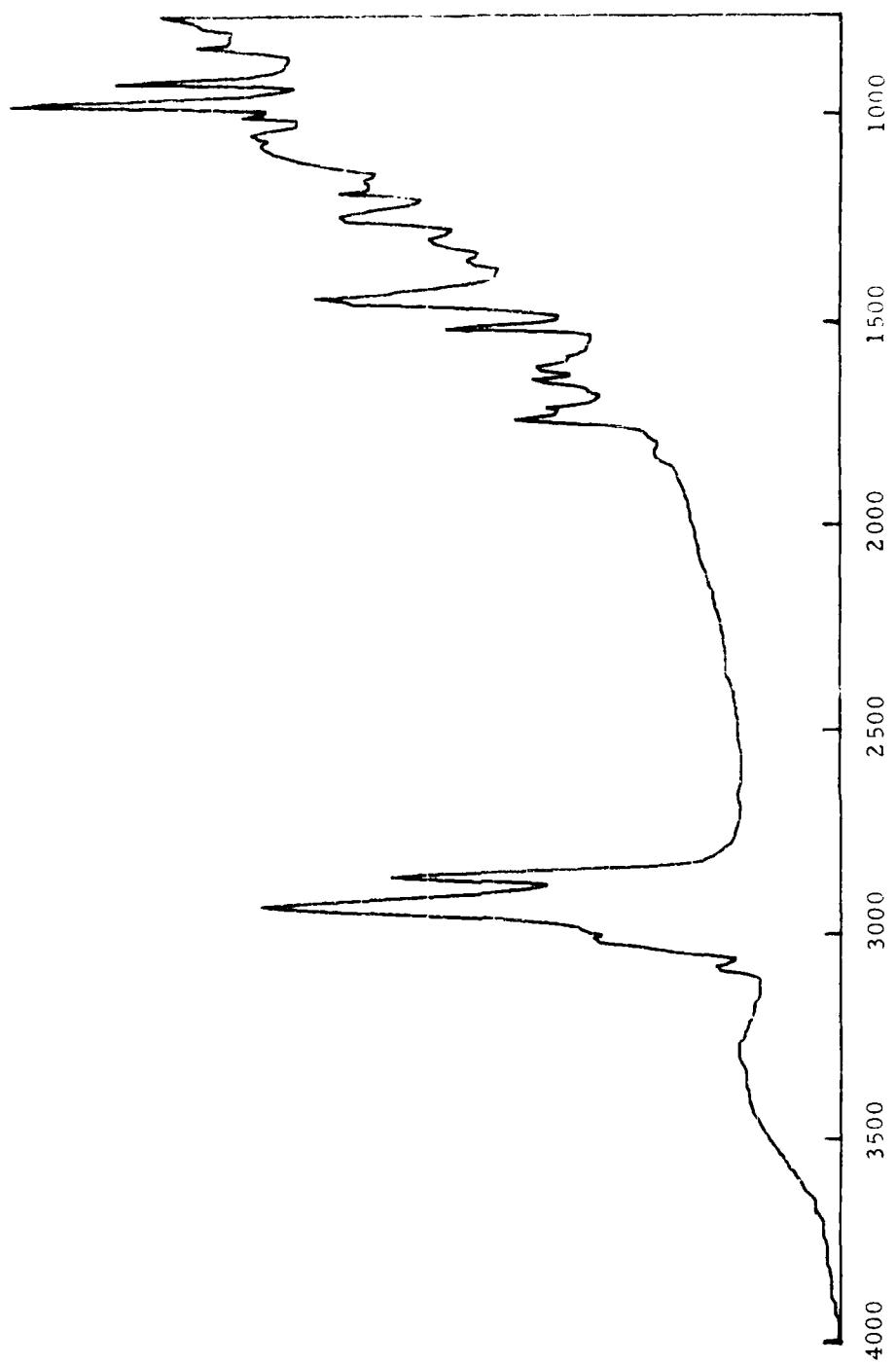
Figure 18. Spectrum of TP-H8156 Aged Zero Time: AP Leached Made with Harrick ATR and Irtran-4.
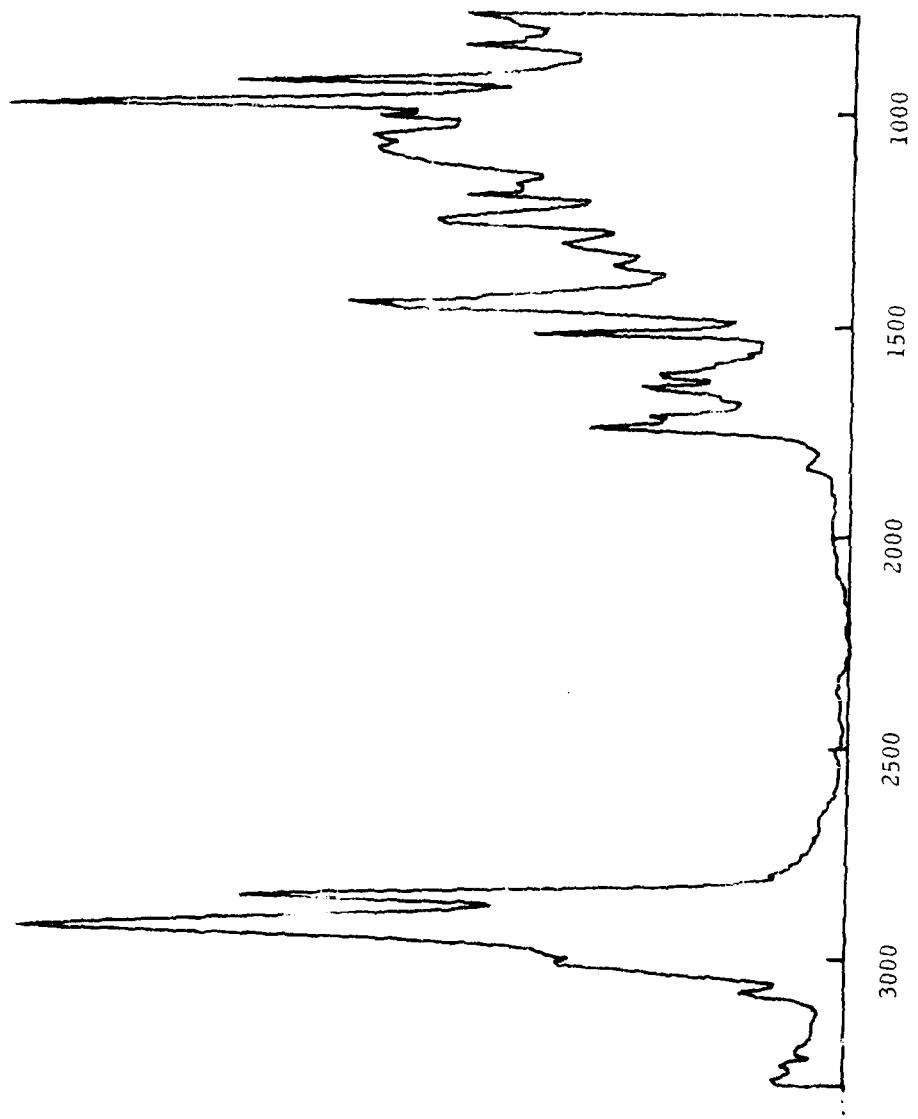
Figure 19. Spectrum of TP-H8156 Aged Zero Time; AP Leached; Al Subtracted. Made with Harrick ATR and Irtran-4.

64
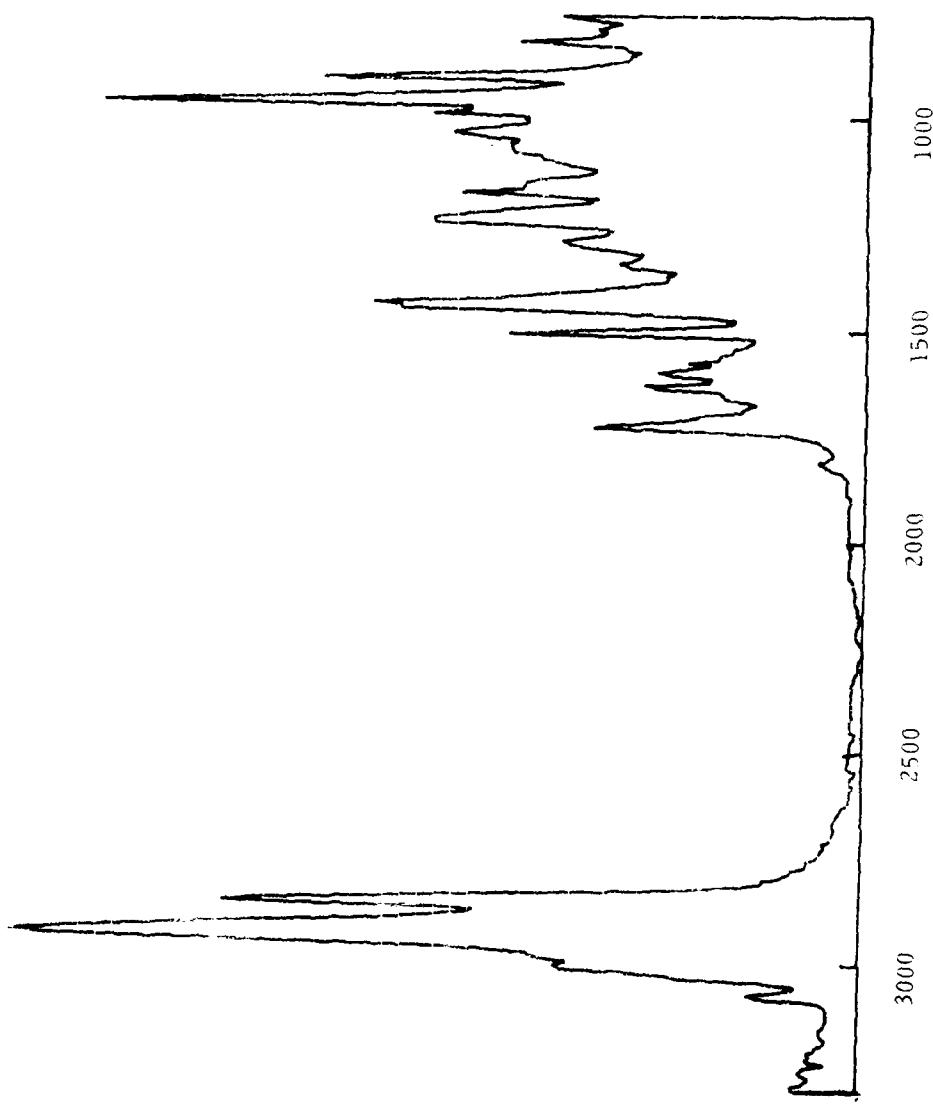
Figure 20.   Spectrum of TP-H8156 Aged 0.5 Month at 150°F; AP Leached, Al Subtracted. Made with Harrick ATR and Irtran-4.
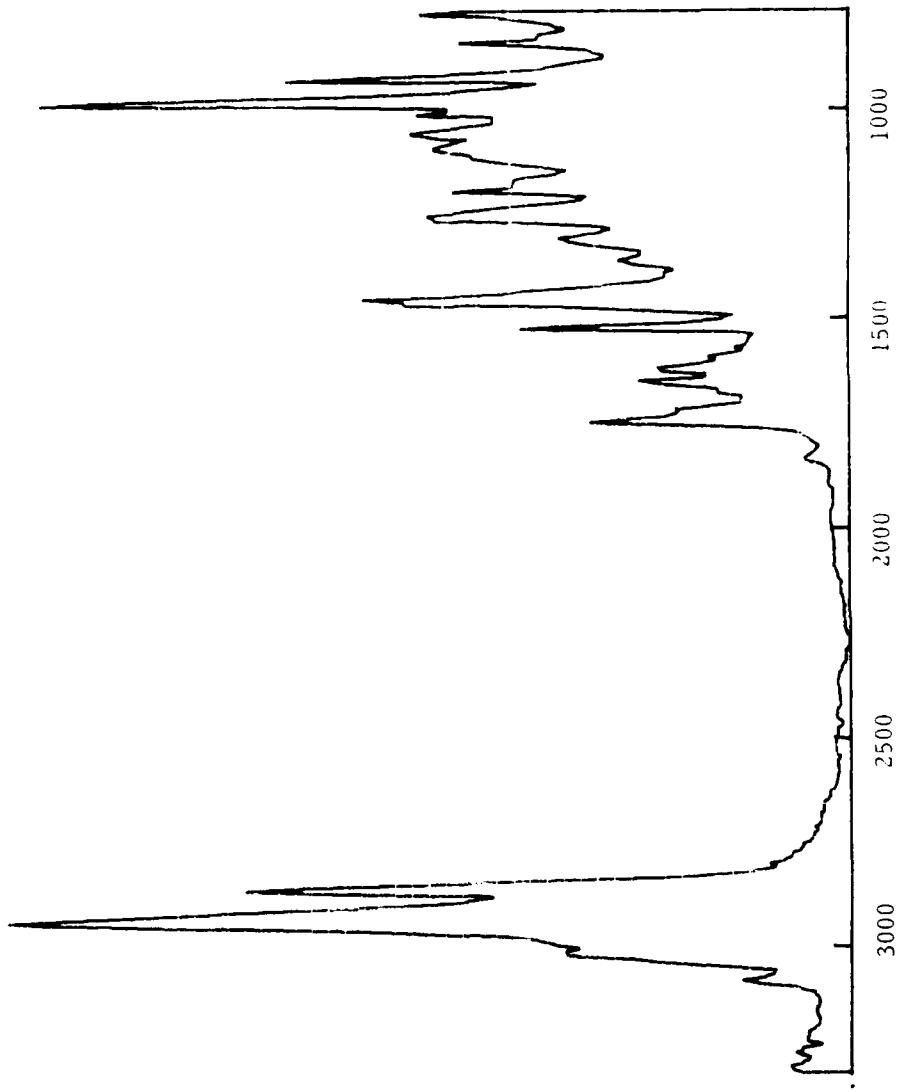
Figure 21. Spectrum of TP-H8156 Aged 1 Month at 150°F; AP leached. Al Subtracted. Made with Harrick ATR and Irtran-4.

66
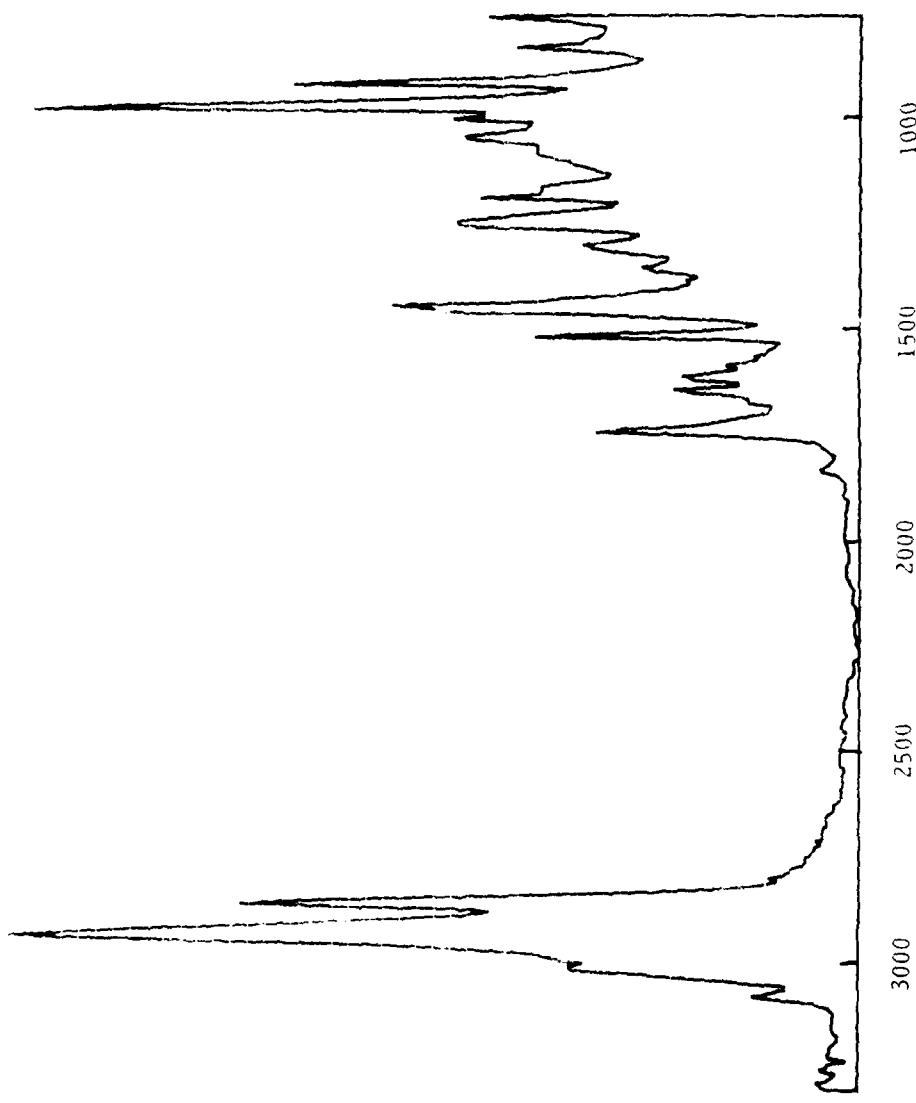
Figure 22. Spectrum of TP-H15156, Aged 2 Months at 150°F: AP Leached Al Subtracted. Made with Harrick ATR and Irtran-4.

67
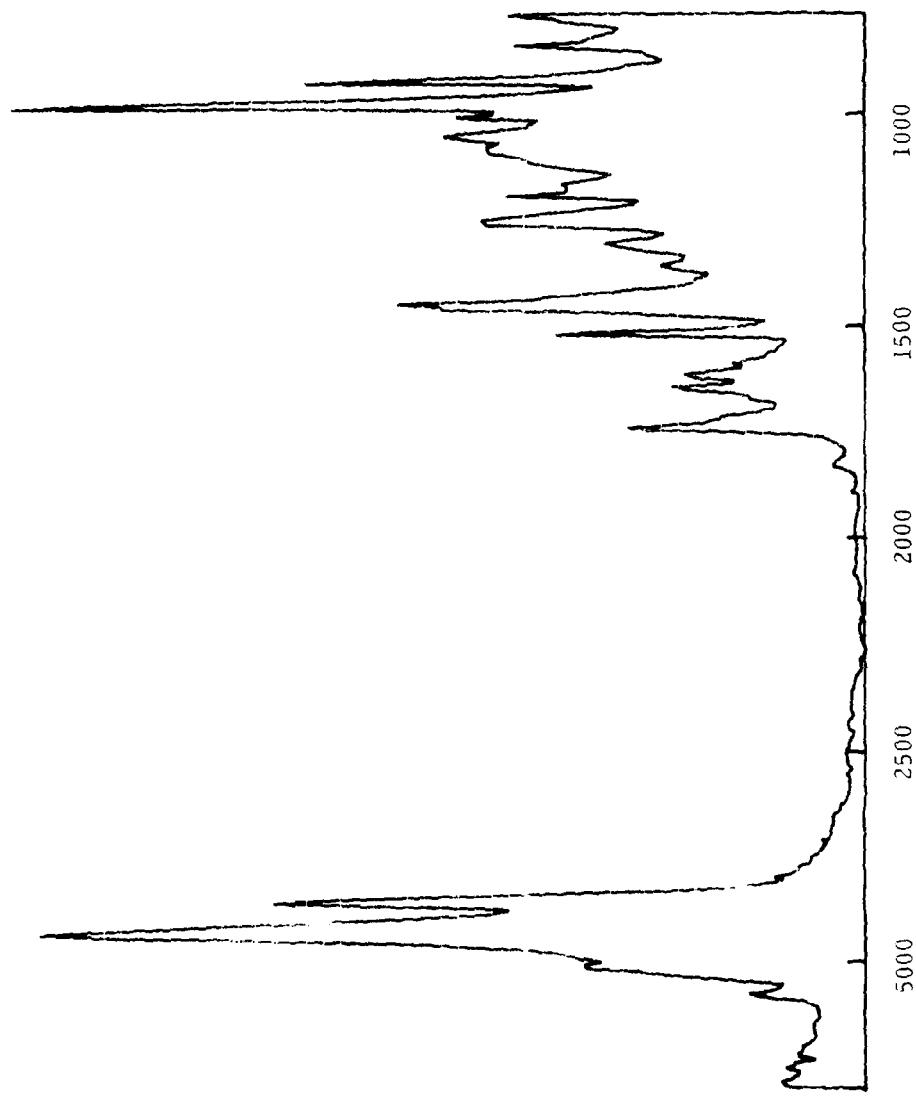
Figure 23. Spectrum of TP-H8156 Aged 3 Months at 140°F; AP Leached, Al Subtracted. Made with Harrick ATR and Irtran-4.

68
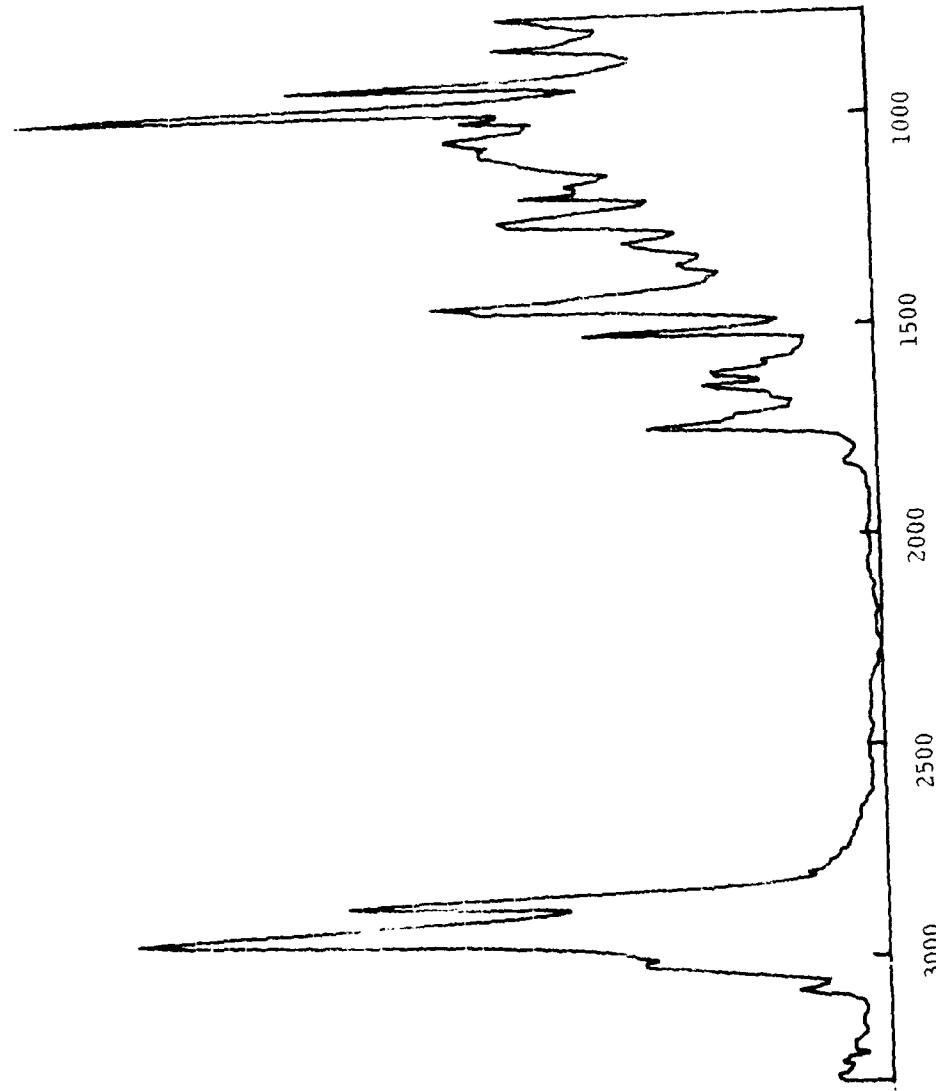
Figure 24. Spectrum of TP-H8156 Aged 6 Months at 150°F; AP Leached. Al Subtracted. Made with Harrick ATR and Irtran-4.

Irtran-4 the peaks in the 2900 cm^{-1} region are considerably larger. Also, the peaks occurring in the region 1700 to 1000 cm^{-1} are also larger, making the measurements of peak height easier and the accuracy of the measurement greater.

Peak heights were measured using the data reduction technique "D" and peaks were normalized, as in other cases, on the peak at 2920 cm^{-1}. Normalized peak height data are given in Table 10 along with correlation coefficients for the peak heights and propellant mechanical properties.

Again, as was found with the spectra made using the germanium and KRS-5 IRE's, there were no correlation coefficients in excess of 0.9. There were, however, four peaks which provided a correlation coefficient of greater than 0.8, and these peaks are plotted against time in Figure 25. Even though there were no exceptionally high correlation coefficients, there is one peak height change (at 910 cm^{-1}) that follows closely the curve shape of the change of modulus with time. Changes in the height of this peak and changes in modulus are plotted against time on Figure 26. Also shown on this plot is the change of peak height with modulus.

3) Observations

Table 11 presents a comparison of the spectral data/mechanical property correlations observed in testing the same propellant aged at two different temperatures and using two ATR units and three iternal reflection elements.

The first thing that one would look for, obviously, is a commonality of peak height changes that correlate with mechanical property changes. Looking at Table 11, there is only one peak height that appears to change with mechanical properties in three out of the four times; this is the peak at 1250 cm^{-1}. There are five peak height/mechanical property correlations that occur in two out of the four sets of data: 1300 cm^{-1}, 1440 cm^{-1}, 1510 cm^{-1}, 1740 cm^{-1}, and 1850 cm^{-1}.

The lack of commonality between the 190° and 150°F aging is somewhat expected since there may well be different chemical reactions occurring at these two temperatures. Why there was not more commonality when the 150°F aged propellant was tested in the various ATR units is not understood. Obviously, it has something to do with the ATR unit and probably, more specifically, it has to do with the type of IRE used. From the data, it certainly appears that the germanium and the Irtran-4 IRE's are having different effects on the spectra and influence peak height to some measurable extent. Another factor that may be influencing the correlations is the torque used to hold the sample against the IRE. Torque for the germanium and Irtran-4 spectra were different; however, within each group, i.e., germanium and Irtran-4, the torque used was a constant: 34 oz-in in the case of Irtran-4 and 40 oz-in in the case of germanium.

70
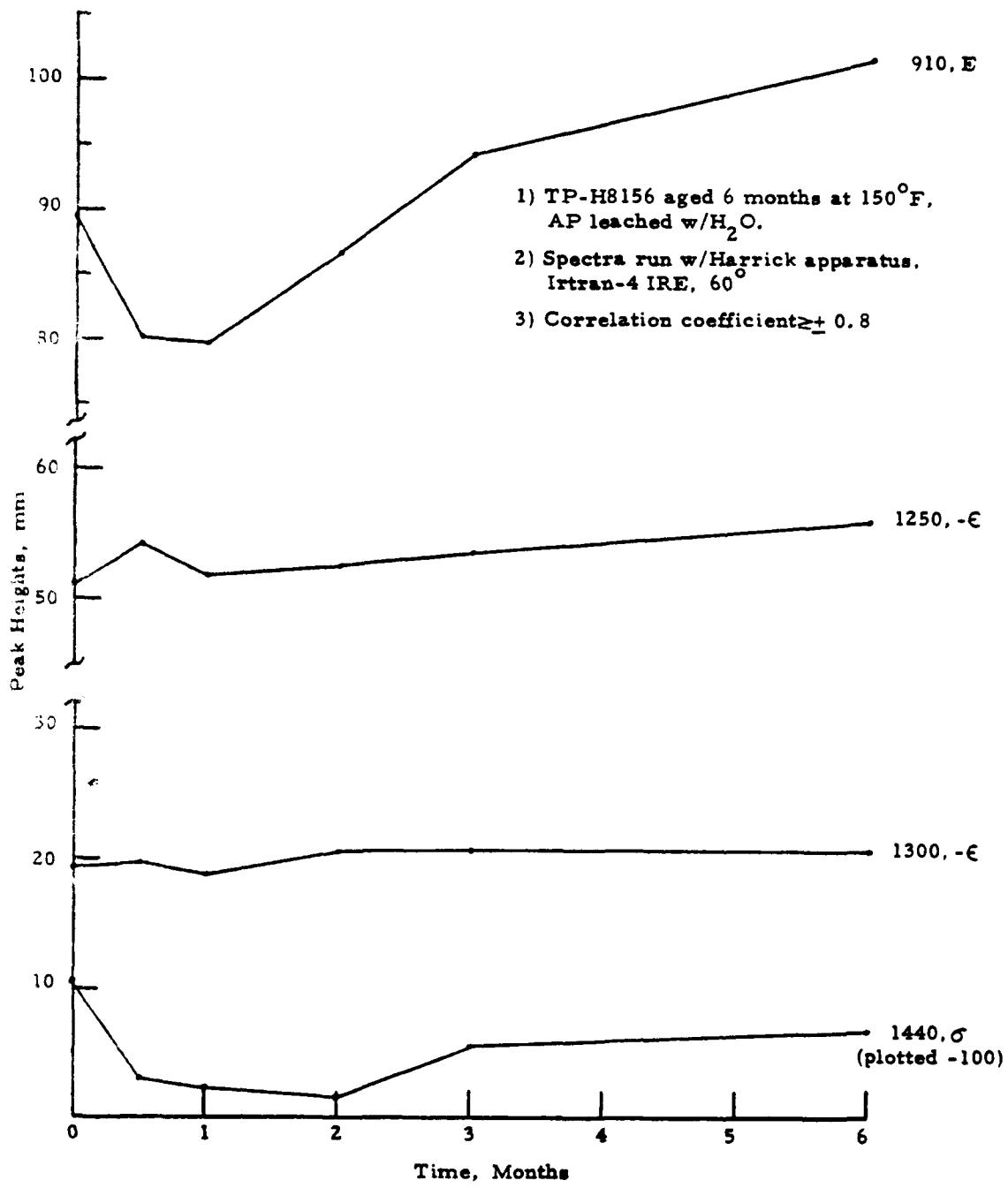
Figure 25. Peak Height Changes vs Time for TP-H8156 Aged 6 Mo. at 150°F.

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TABLE 10

<u>DATA CORRELATIONS - SPECTRAL PEAK HEIGHTS FOR TP-H8156</u>
<u>AGED 6 MONTHS AT 150°F WITH MECHANICAL PROPERTIES</u>

Wave No., cm⁻¹	Age Time, Months						Correlation Coefficients		
	Φ Mo.	.5 Mo.	1 Mo.	2 Mo.	3 Mo.	6 Mo.	E	σ	ε
2920	156.9	156.9	156.9	156.9	156.9	156.9	Normalization Peak		
2850	108.6	107.9	101.6	107.0	100.4	101.2	-.2209	-.0666	-.4414
1740	56.7	58.8	56.5	60.3	56.1	57.9	-.1185	-.2954	-.4275
1710	30.6	19.1	24.0	15.2	20.7	22.0	.2860	..6276	.7151
1640	21.6	21.8	21.2	21.1	21.1	20.3	△ Insufficient 1st 5 No's.		
1610	16.4	16.4	16.5	16.8	16.8	17.9	△ Insufficient 1st 5 No's.		
1510	67.6	73.0	67.9	70.8	68.3	70.3	-.1046	-.3682	-.4527
1440	110.2	102.9	102.2	101.5	105.3	106.7	.7096	.8893	.2796
1350	12.2	11.9	11.0	11.9	11.1	11.2	-.0396	.1139	.3622
1300	19.4	19.8	18.8	20.5	20.6	20.3	.4079	.0757	-.8294
1250	51.1	54.2	51.9	52.5	53.4	55.8	.5080	.1499	-.8007
1190	34.0	42.3	38.8	41.4	39.3	39.8	-.3090	-.6558	-.6498
1170	13.0	22.3	18.6	22.3	18.8	19.9	-.2947	-.6364	-.6695
965	135.4	121.7	130.0	141.9	156.2	166.5	.7921	.5752	-.7232
910	89.7	80.1	79.8	86.8	94.1	101.5	.9324	.7702	-.5991
Norm.factor	1.0309	1.0377	1.0000	1.0123	1.0343	1.1175			

NOTES:

1) Spectra run in Harrick apparatus w/Irtran-4 IRE at 60° angle and 24 oz-in torque.

2) Aluminum spectrum subtracted.

3) AP leached w/H_2O at 35°-40° C for 21 hours.

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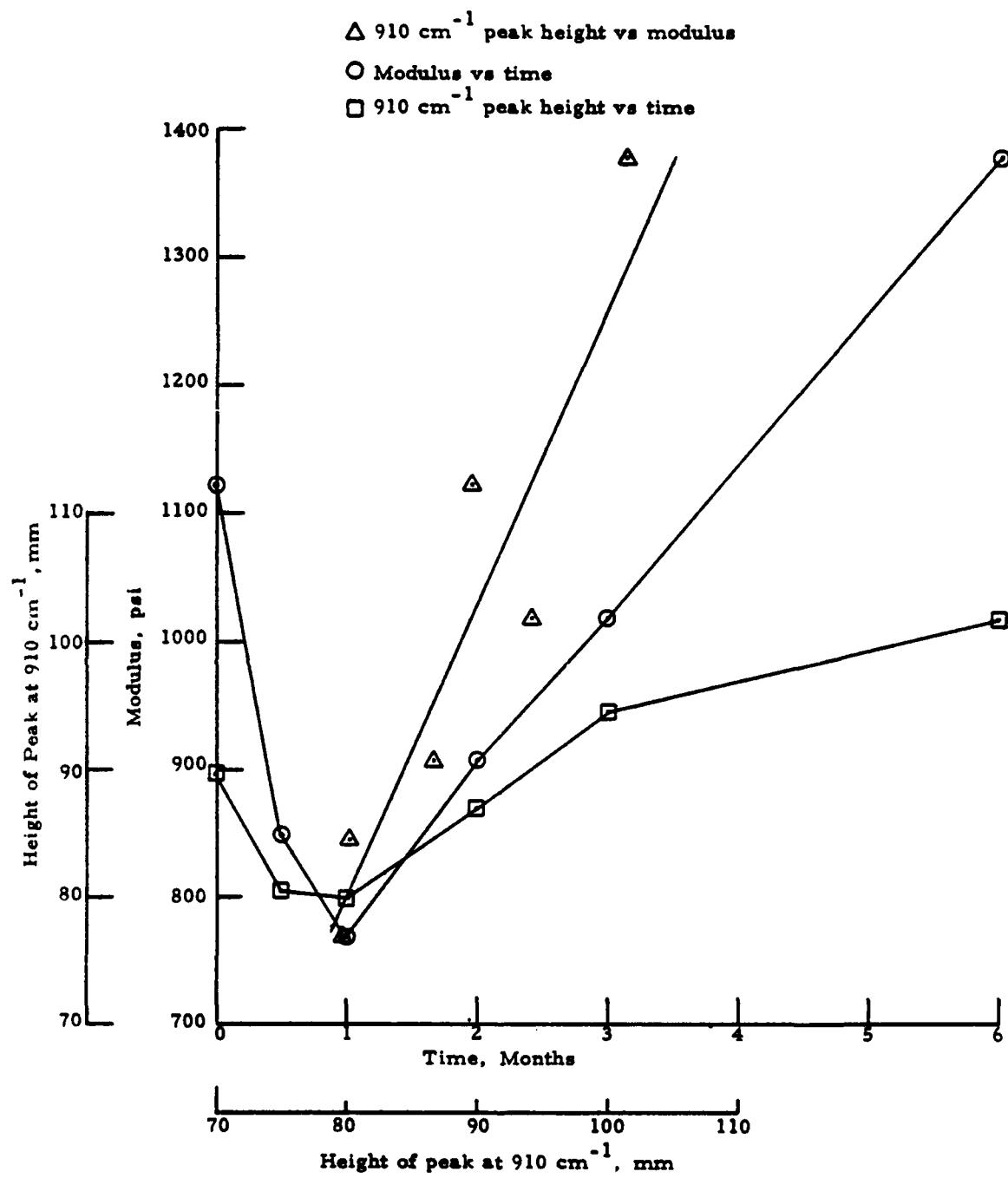
Figure 26. Relationship of 910 cm^{-1} Peak and Modulus
To Time and To Each Other

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TABLE 11

SUMMARY OF SPECTRAL DATA/MECHANICAL
PROPERTY CORRELATIONS (WHERE COEFFICIENT $\geq \pm 0.8$)

190°F Aging	150°F Aging		
KRS-5	KRS-5	Ge	Irtran-4
825 cm^{-1}			
			910 cm^{-1}
		965 cm^{-1}	
1180			
1250		1250	1250
1300			1300
		1350	
	1440		1440
1510	1510		
1710			
1740		1740	
2850		2850	

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4) Effect of Angle of Incidence on Transmitted Energy

The effect of angle of incidence, mirror alignment and focus on transmitted energy was evaluated. The mirrors of the Harrick Scientific Company 4X beam condenser were aligned with the apparent angle of incidence fixed at 60°, and aligned and focused a second time with the apparent angle of incidence set at 35°. From each of these points, i. e., 60° and 35°, the angle of incidence was changed to cover the entire span from 35° to 60°. The maximum amount of energy transmitted in the single beam black body curve of the FTS-10 was recorded. These data are plotted on Figure 27. A review of the data reveals that the amount of energy transmitted at the various angles of incidence is not a constant and, further, that the amount of energy transmitted through the internal reflection element is a function of where the alignment and focus of the mirrors was made, as well as the angle of incidence. With alignment and focus made at an apparent angle of incidence of 60°, a maximum amount of energy is transmitted through the internal reflection element. Alignment and focus made at an apparent angle of incidence of 35° resulted in a lesser total energy passing through the IRE. On the basis of these data, and the general appearance of the spectrum, this led to selection of an apparent angle of incidence of 60° as the angle to use in obtaining the propellant spectrum.

Before proceeding further, it would be well to explain the "apparent" angle of incidence that is being used. The Harrick Scientific Company 4X beam condenser has a vernier dial to set the angle at which the infrared light beam strikes the rectangular aperture of the internal reflection plate. This dial is correct only when the light beam strikes the entrance bevel at normal incidence, i.e., at 45° setting for 45° plates, 30° setting for 30° plates, or 60° setting for plates. When the external angle is changed from normal incidence because of refraction, the internal angle changes less, viz., the change is Θ/n. Thus, a 45° angle plate at 45° setting operates at 45°, while, if the sample plate is at the internal angle is only $48\ 3/4^{\circ}$. A table of the actual internal angles for various externally set angles is given in Table 12. This table shows actual angles of incidence for two set angles for the three materials that we have evaluated, KRS-5, Irtran-4, and germanium. All plates that are being evaluated have an entrance angle of 45°.

Thus, when reference is made to a 60° angle of incidence, the reference is to the angle set on the vernier dial and it is not a reference to the internal angle of reflection. The reference is made this way for convenience only, because it is an angle that can be read from the ATR unit's vernier dial.

5) Effect of Angle of Incidence on Transmitted Energy Curve

Because the FTS-10 spectrophotometer operates in a stored reference mode, it was important to identify the conditions under which a reference spectrum
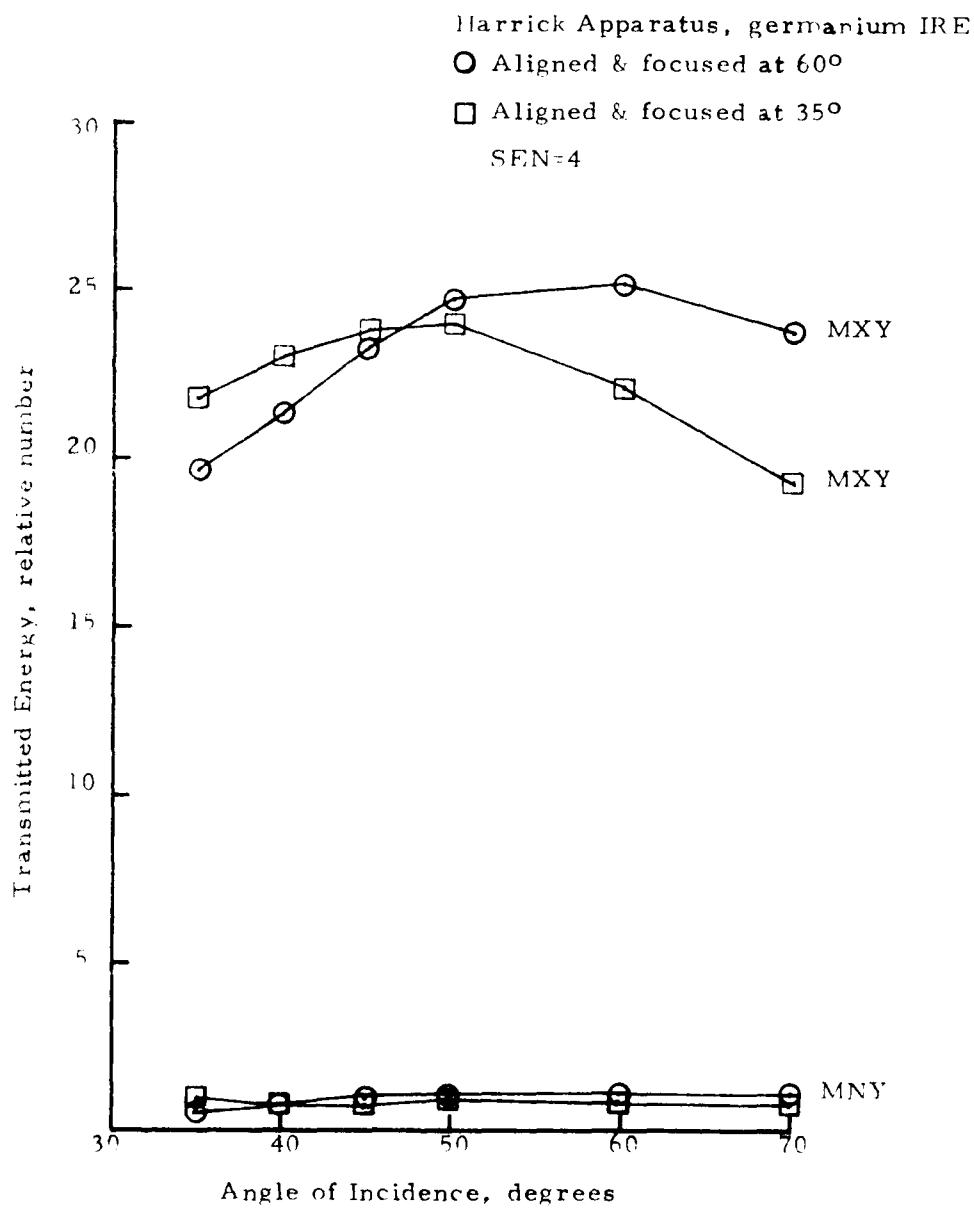
Figure 27. Effect of Angle of Incidence on Transmitted Energy

TABLE 12

ACTUAL ANGLE OF INCIDENCE FOR SET ANGLES

Plate	n	Actual Angle When Set At	
		45°	60°
KRS-5; Irtran-4, 45°	2.4	45°	$51^{\circ}15'$
KRS-5; Irtran-4, 60°		$53^{\circ}45'$	60°
Germanium, 45°	4.0	45°	$48^{\circ}45'$
Germanium, 60°		$56^{\circ}15'$	60°

could be made and still be usable with a sample spectrum. Several single
beam reference spectra were collected at angles of 35°, 45°, and 60°, and
the general curve shape of these spectra were compared. Examination of these
single-beam spectra reveals that there were minor differences in the shapes
of the single-beam curves, such that reference spectra made at 45° and 60°
with a germanium internal reflection element are interchangeable but that a
reference spectrum made at 35° is sufficiently unlike spectra made at 45° or
60° that it should not be used with sample spectra made at 45° or 60°.

In studying these spectra, it was also found that germanium "cuts off" at
845 cm^{-1}. This "cut off" results in a discontinuity in absorption spectra between
845 and 845 cm^{-1}. The energy level through the IRE in this region is too low for
the computer in the FTS-10 to differentiate between noise and signal, even though
a large number of scans have been employed. If the FTS-10 parameter NLV is
set to 0.1, rather than its usual value of 1.0, the absorption spectrum discontinu-
ity disappears, but the data in this low energy region is highly questionable
because the computer has been severely limited in its ability to discriminate
between noise and signal. Under these conditions, absorptions in the region from
900 to 800 cm^{-1} are highly suspect. Therefore, in using germanium as the IRE,
it was a general practice to ignore spectral information lower than 900 cm^{-1}.

Another interesting feature was noted in these spectra. There is a small
absorption at 2920 and 2850 cm^{-1} in the single beam spectrum. This is the
CH_x region and almost all organic materials have some absorption in this
region. It was initially felt that there was grease or oil on the germanium IRE,
however, the IRE was washed repeatedly with methylene chloride to remove any
organic material. The absorptions persisted, however, so they can only be
attributed to absorptions of the hard plastic material IRE holder. This hard
plastic is Delrin and it would have an absorption in the CH_x regions. Because
the same holder is always used, the absorption in this region will be the same,
whether it is a reference spectrum or a sample spectrum. In the computation
of an absorption spectrum from two single beam spectra (one reference and one
sample), the sample spectrum is divided by the reference spectrum and so long
as the absorptions in this region are of the same magnitude, the effect will cancel
out and there will be no disturbance to the sample's absorption in this region.

6) Studies with Germanium IRE

A series of tests was run to determine the effect of torque holding the
sample against the IRE and the angle of incidence on the spectra thus produced.
These tests were run first using a germanium IRE. One set of tests was run in
which the angle of incidence was set at 60° and the amount of torque on the sample
holder bolt increased from 16 oz-in to 50 oz-in. Then a second set of tests was run

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in which the torque was maintained at a constant 50 oz-in and the angle of incidence of the infrared light varied from 55° to 60°. In all of these tests, a single propellant specimen was used so that composition of the specimen was not a variable in the experiments.

Torque on the sample was set at 16 oz-in, the angle of incidence set at and an absorption spectrum made. The second spectrum was run at 24 oz-in again at a 60° angle of incidence. Succeeding spectra were made at 32, 40, in torque. With the torque on the sample undisturbed, the angle of was then decreased to 45° and a spectrum made; and then the angle decreased to 35° and the final spectrum made. A single reference spectrum was all of the sample spectra so that the shape of the reference spectrum not a variable in this set of experiments.

In order to evaluate the effect of the variables on the peak heights, the procedure was used. Heights of peaks at the end of the spectra and middle were measured; these peaks were 2920, 1440, and 965 cm^{-1}. data reduction technique was employed. Because the peak at 2920 was selected as the normalizing peak, the ratio between this peak and other two was calculated as a means of determining whether torque and angle of incidence had any effect upon the various spectra and whether the was uniform from one end of the spectrum to the other. All measured and calculated data are displayed in Table 13.

A single set of conditions, 50 oz-in of torque at 60° angle of incidence, selected as a baseline and the percent change in the ratios 1440/2920 and 1040/2920 were computed against this baseline.

Based on these data, several very interesting observations can be made. effect of torque on variations in the spectrum from one end to the other have effect than the variations in the angle of incidence at a constant torque. variation in peak heights is not constant from one end of the spectrum to the for a change either in torque or in angle of incidence. Generally, for a change in torque at constant angle, there is more change in the low wave number of the spectrum than there is in the middle of the spectrum. Another interesting observation is that baseline drift generally decreases as torque increases at a constant angle of incidence. This says that there will be fewer errors in measuring peak height at higher torque values, therefore spectra presented in the discussion of the Task 1 work were all run at a high torque value, i.e., 40 oz-in.

The effect of angle of incidence was considerably more pronounced than of torque. At low angle of incidence, i.e., 35°, the changes in the peaks from one end of a spectrum to the other was quite pronounced, baseline drift increasing drastically as the angle of incidence was decreased to 35°. This says that, as a general rule, a high angle of

TABLE 13

EFFECT OF TORQUE AND ANGLE OF INCIDENCE ON SPECTRA MADE USING GERMANIUM IRE

Test No.	Torque, oz-in	∠Incidence, Degrees	Type Al Subtracted	Peak Heights, mm			$\frac{1440}{2920}$	$\frac{965}{2920}$	(1) Δ because of torque at constant angle		(2) Δ because of angle at constant torque		(3) Δ because of subtract at constant torque and angle	
				$\frac{2920}{cm^{-1}}$	$\frac{1440}{cm^{-1}}$	$\frac{965}{cm^{-1}}$			$\frac{1440}{2920}$	$\frac{965}{2920}$	$\frac{1440}{2920}$	$\frac{965}{2920}$	$\frac{1440}{2920}$	$\frac{965}{2920}$
1	16	60	-	55.4	39.5	145.3	0.7130	2.6227	3.45%	10.80%				
2	24	60	-	64.6	44.7	167.6	0.6920	2.5944	0.41%	9.60%				
3	32	60	-	65.6	47.7	167.8	0.7271	2.5579	5.50%	8.06%				
4	40	60	-	68.0	49.0	165.3	0.7206	2.4309	4.56%	2.70%				
5	50	60	-	71.1	49.0	168.3	0.6892	2.3671	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
6	50	45	-	68.3	49.9	152.0	0.7306	2.2255			6.01%	-5.98%		
7	50	35	-	74.0	54.7	141.2	0.7392	1.9081			7.25%	-19.39%		
8	50	60	Foil	83.2	56.9	193.9	0.6839	2.3305					-0.77%	-1.55%
9	50	60	Powder	76.6	53.2	180.9	0.6945	2.3616					0.77%	-0.23%

NOTES:

1) $\Delta = \dfrac{\text{Value} - \text{Value at 50 oz-in}}{\text{Value at 50 oz-in}} \times 100$

2) $\Delta = \dfrac{\text{Value} - \text{Value at } 60^\circ}{\text{Value at } 60^\circ} \times 100$

3) $\Delta = \dfrac{\text{Value} - \text{Value at 50 oz-in \& } 60^\circ}{\text{Value at 50 oz-in \& } 60^\circ} \times 100$

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incidence will make better spectra than a low angle of incidence. It is for this reason that the spectra run using the germanium IRE, and presented in the Task 1 discussion, were made at an angle of incidence of 60°.

The overall effect of torque and angle of incidence on the maximum absorptive value in the various spectra are plotted on Figure 28. This maximum absorptive value is in the "MXY" displayed by the FTS-10. This plot shows that as the torque on the sample is increased at a constant angle of incidence, the maximum absorptive value increases. It also shows that, as the angle is decreased at a constant torque value, the maximum absorption also increases; however, this increase is due to upward baseline drift and results in a net decrease in the peak height with the increased absorption due primarily to baseline drift, a problem that we would like to avoid. The condition of high torque at a high angle of incidence seems to be about the best set of conditions for obtaining spectra with a germanium IRE.

One additional set of experiments was performed to measure the effect of subtracting the spectral influence of aluminum from the spectra of propellant. To that end, the spectrum of aluminum foil was obtained at an angle of incidence of 60° and this spectrum subtracted from the spectrum obtained under the test number 5 conditions, as displayed on Table 13. Also, the spectrum of aluminum powder was obtained at an angle of incidence of 60° and this spectrum subtracted from the propellant spectrum also at the test number 5 conditions (on Table 13. The two spectra of aluminum, one made from powder and one made from foil, are displayed on Figures 29 and 30, respectively. In making the spectrum of aluminum powder, it was found that changing the torque from 20 oz-in to 30 oz-in made no difference in the quality of the spectrum and, since the spectrum made at 20 oz-in had less noise, that spectrum was used for the subtraction.

Note on the spectrum of aluminum foil, Figure 30, that there is a small absorption in the CH_x region and it must be due to some organic material on the surface of the aluminum foil, although the aluminum foil was degreased with methylene chloride and dried in an oven to remove moisture. Whatever this organic material is, it's quite insoluble and well deposited on the aluminum foil, but since the absorption was quite small and in these experiments we required only comparative data, not absolute, the effect of this small absorption in the CH_x region was ignored.

Note on the spectrum of aluminum powder, Figure 29, that there is a slight negative absorption in the CH_x region. Since this is a negative absorption, it denotes that, when the sample single beam spectrum was taken, there was more of an absorption in this region than there had been in the reference single beam spectrum, and, since in the FTS-10 computer an absorption spectrum is created by dividing the sample single beam spectrum by the reference single beam spectrum, this turned out to be a negative absorption in the CH_x region. Because this absorption is quite small, and again because we were after comparative data, not absolute data, this effect was ignored.

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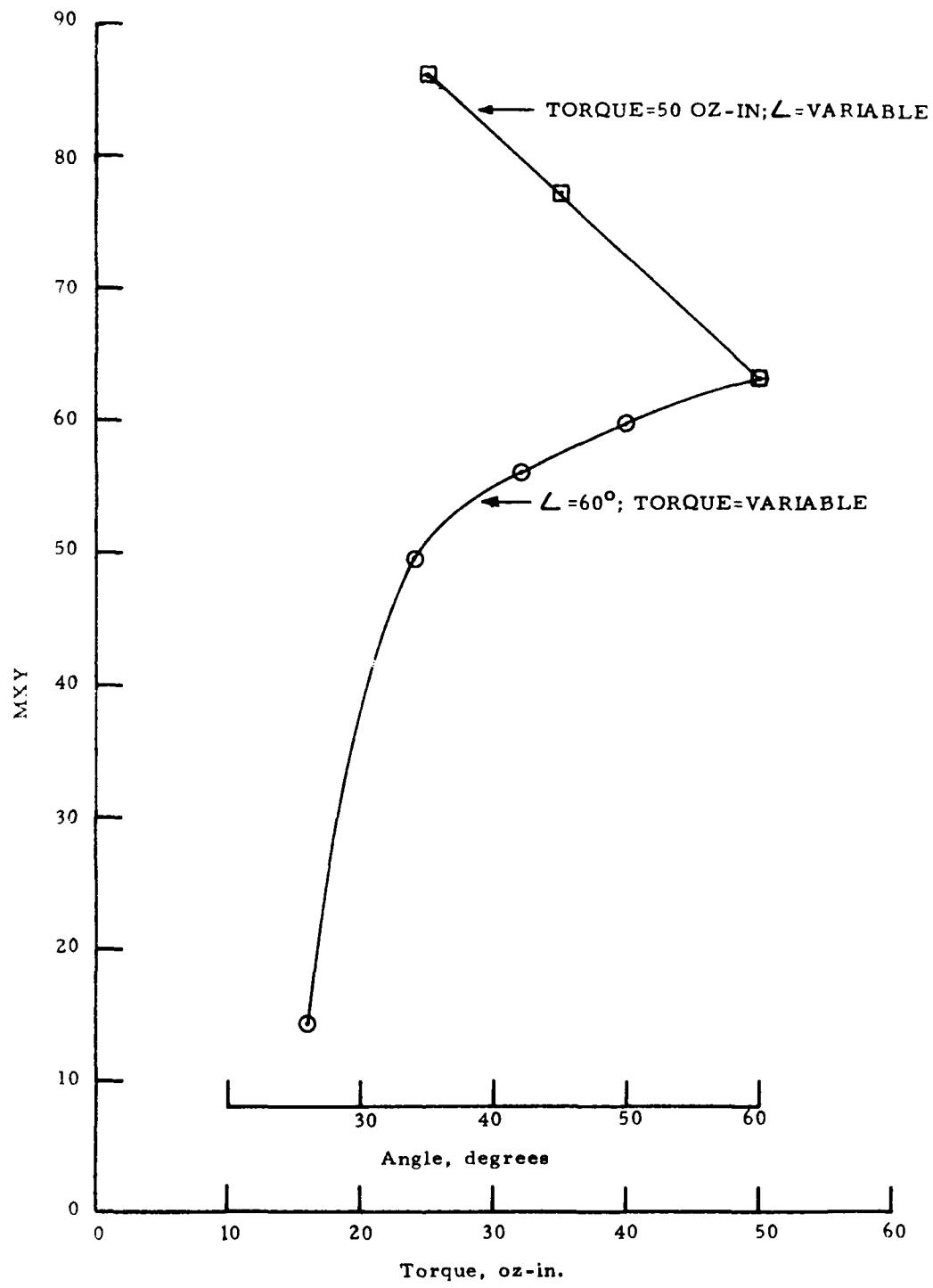
Figure 28. Effect of Torque and Angle of Incidence on Maximum Absorptive Value.

82
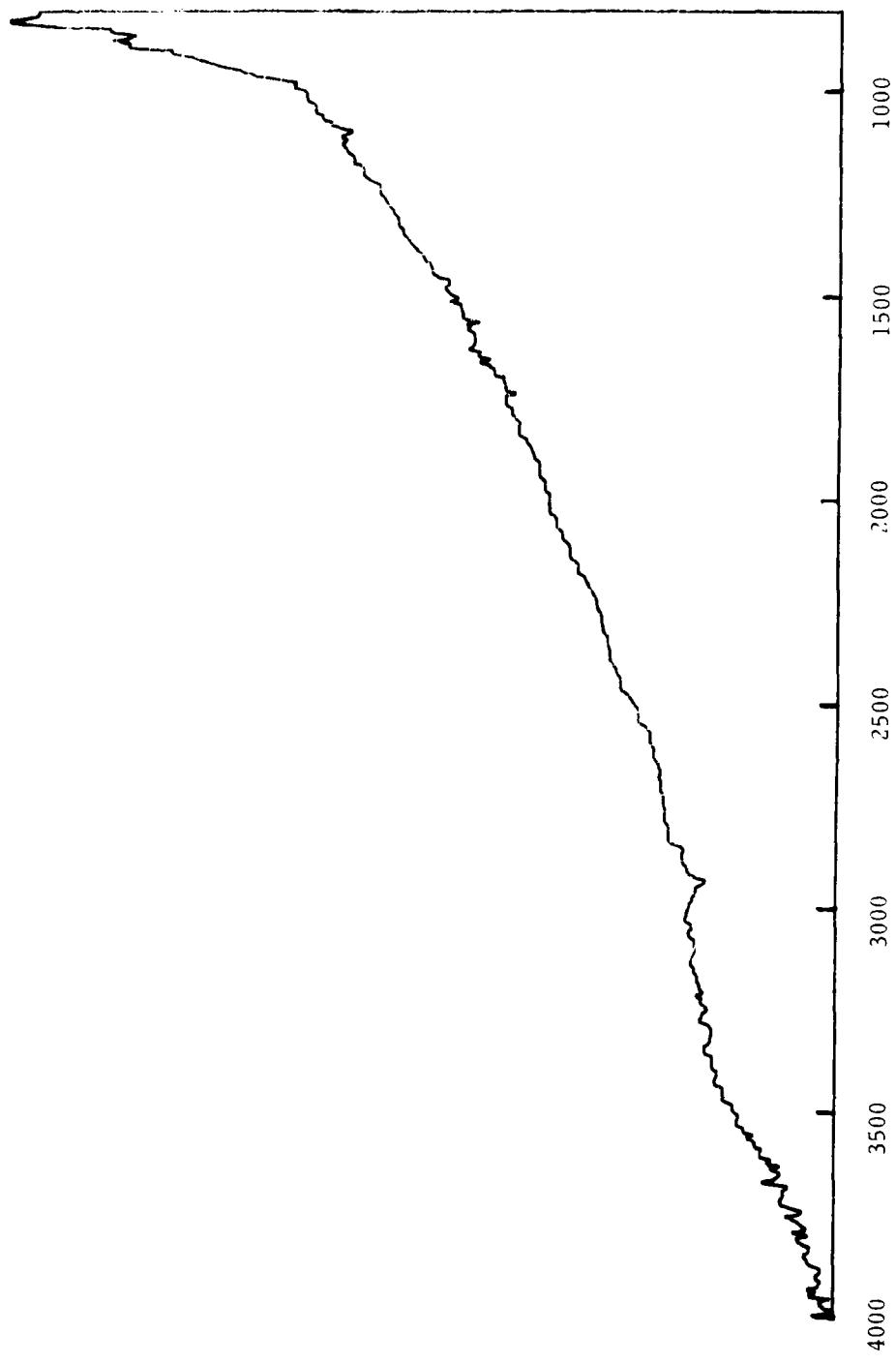
Figure 29. Spectrum of Aluminum Powder. Made with Harrick ATR and Ge.

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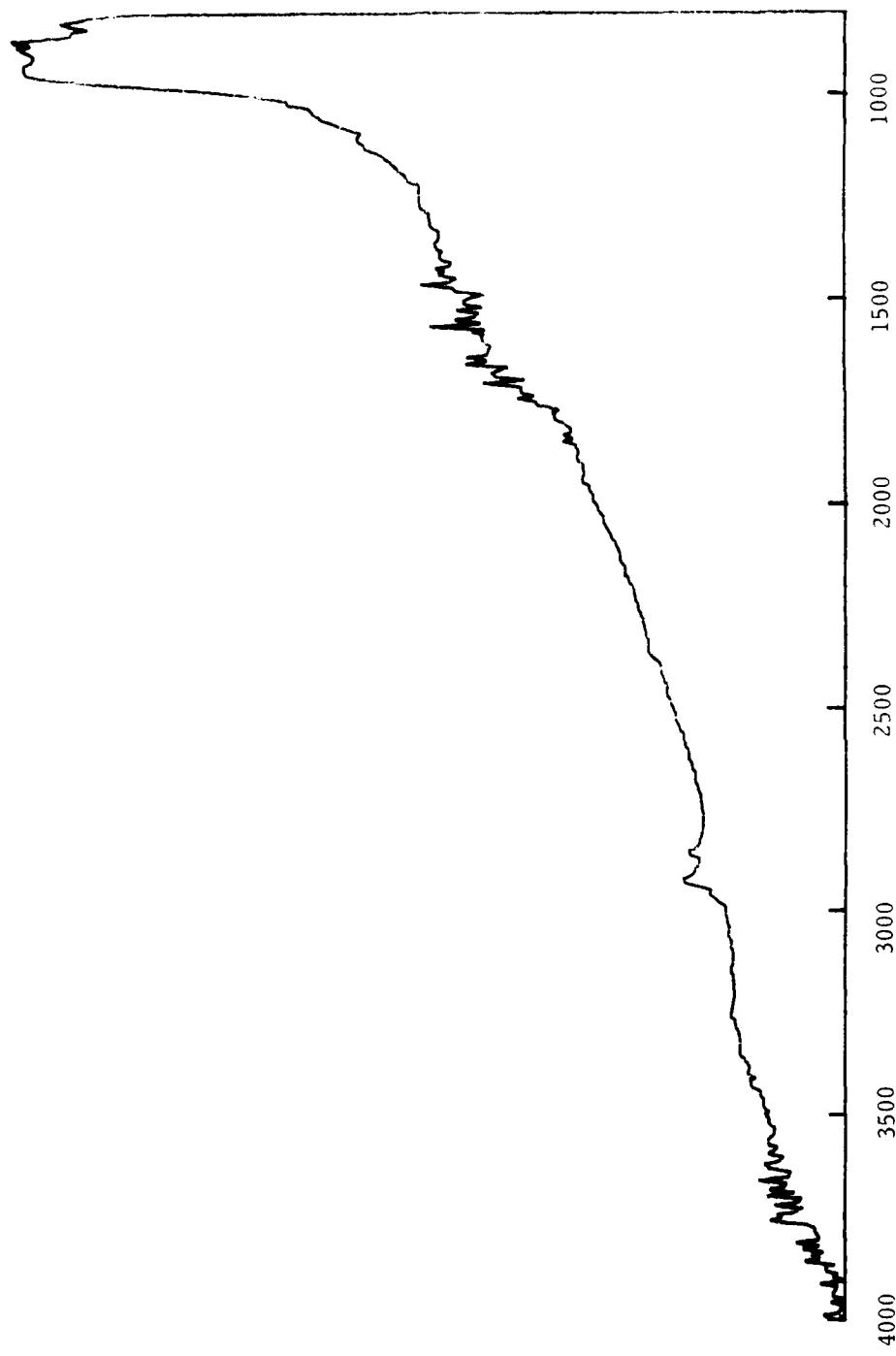
Figure 30. Spectrum of Aluminum Foil, Made with Harrick ATR and Ge.

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With reference to Table 13, the effect of subtracting the two aluminum spectra from the propellant spectrum can be seen by examining the data recorded for tests 8 and 9. The percent changes in the two ratios, 1440/2920 and 965/2920, are very small when compared to the selected baseline conditions, i. e., test number 5. Aluminum powder, overall, changed the two important ratios less than the aluminum foil did, and this is probably due to the difference in the general shape of the two aluminum spectra and may be due, in small part, to the small absorptions, positive and negative, that occurred in the two spectra in the CH_x region.

Since aluminum is present in propellant in the powder form and the powder spectra had less of an effect on the two peak ratios, the subtraction of aluminum from the spectrum of propellant should always be accomplished using the spectrum of powdered aluminum rather than aluminum foil.

7) Studies with Irtran-4

A set of tests identical to that just described for the germanium IRE was conducted using the Irtran-4 IRE (Irtran-4 is zinc selenide, ZnSe). Data from these tests of the effect of torque and angle of incidence on spectra made using Irtran-4 are presented in Table 14. In these experiments a single sample of propellant was used. Torque on the sample holder was set at 16 oz-in and the angle of incidence varied from 35° to 70°. Spectra were taken at 35°, 45°, 60° and 70°. The angle of incidence was then returned to 60° and held constant while the torque on the sample holder was increased from 16 oz-in to 24, 32 and 40 oz-in; spectra were made at each of the specified torque values.

8) Conclusions

The effect of the angle of incidence at a constant torque level on the spectra was as follows:

A) The baseline drift increased as the angle decreased.

B) The peak height at 2920 cm^{-1} increased as the angle decreased from 70° to 45°.

C) The peak height at 965 cm^{-1} increased as the angle decreased from 35° to 70°.

The conclusion from these observations is that when using Irtran-4, a high angle of incidence is preferable to a low angle of incidence.

The effect of torque at a constant angle of incidence on the spectra can be summarized as follows:

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TABLE 14

EFFECT OF TORQUE AND ANGLE OF INCIDENCE ON SPECTRA MADE USING IRTRAN-4 IRE

Test No.	Torque, oz-in	Angle, Degrees	Peak Heights, mm			1440/2920	965/2920	(1) Δ because of angle at constant torque		(2) Δ because of torque at constant angle		(3) Δ Upon return to 60°	
			2920 cm⁻¹	1440 cm⁻¹	965 cm⁻¹			1440/2920	965/2920	1440/2920	965/2920	1440/2920	965/2920
1	16	35	133.9	50.5	61.4	0.3771	0.4586	-17.65%	-26.94%				
2	16	45	149.8	60.7	62.5	0.4052	0.4172	-11.51%	-33.54%				
3	16	60	137.8	63.1	86.5	0.4579	0.6277	0.00%	0.00%				
4	16	70	132.2	63.1	100.2	0.4599	0.7303	0.44%	16.35%				
5	16	60(return)	144.7	64.6	80.5	0.4464	0.5563			0.00%	0.00%	0.00%	0.00%
6	24	60	145.8	66.7	79.3	0.4575	0.5439			2.49%	-2.23%	-2.51%	-11.37%
7	32	60	155.9	70.8	80.3	0.4541	0.5151			1.72%	-7.41%		
8	40	60	127.9	61.9	101.3	0.4940	0.7920			8.42%	42.37%		

NOTES:

1) $\Delta = \dfrac{\text{Value} - \text{Value at }60^{\circ}}{\text{Value at }60^{\circ}} \times 100$

2) $\Delta = \dfrac{\text{Value} - \text{Value at 16 oz-in (return)}}{\text{Value at 16 oz-in (return)}} \times 100$

3) $\Delta = \dfrac{\text{Value (return)} - \text{Value (original)}}{\text{Value (original)}} \times 100$

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A) The upward drift of the baseline generally decreases as torque is increased.

B) The peak height at 2920 cm^{-1} increases as torque is increased from 16 to 32 oz-in and then unexpectedly decreases at 40 oz-in.

C) The peak height at 965 cm^{-1} is virtually constant from 16 to 32 oz-in and then increases unexpectedly at 40 oz-in.

Based on these observations, it was concluded that a torque value of at least 24 oz-in would be preferable to any lower value. Because Irtran-4 is a fairly soft material, it is easily deformed and so exceedingly high torque values would be inadvisable as this would destroy the surface of the Irtran-4 IRE and, thus greatly reduce its ability to transmit light. A value of 24 oz-in seems to be a reasonable trade-off between low amount of baseline drift and the risk of deforming the Irtran-4 internal reflection element.

There are some comments that can be made concerning the overall effect of Irtran-4 of the quality of the spectra.

A) The general shape of the spectra is less like a transmission (see-through) spectra than the spectra produced by a KRS-5 or a germanium IRE.

B) The baseline drift problem that we are experiencing is similar to that found with KRS-5 and of about the same magnitude. The baseline drift problem can be corrected here as it is in the KRS-5 by the subtraction of the spectrum of aluminum.

C) Irtran-4 scratches less easily than KRS-5 and, for that reason, it is certainly preferable to KRS-5.

D) The angle of incidence used is difficult if not impossible to reproduce. A review of the results of tests 3 and 5 on Table 14 will reveal this fact. Trying to return to an angle of 60° and reproduce the spectra produced previously at 60° resulted in a considerable change in the two peak ratios that were calculated, with the ratio 965/2920 being changed by 11%. This is a large change and may in some cases be the same order of magnitude as the change in peak height with propellant mechanical properties. In light of this and the observed effect of the angle on the ratio of peak heights, from one end of the spectrum to the other, it would be desirable to use a fixed angle ATR unit so that the data can be used quantitatively.

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Removal of Interfering Chemical Specie

Several propellant ingredients have an undesirable effect on the IR spectra of solid propellant. Materials such as AP and ester-type plasticizers have strong IR spectra of their own and they mask the IR spectrum of the propellant's organic binder. Materials such as Al, Zr, C and ZrC do not have IR spectra, but they do disperse IR energy and, thus, do have an effect on the spectrum of whole propellant. This effect manifests itself as upward drift of the spectral baseline; and, if the drift is severe enough, the spectrum loses its quantitative character.

Two techniques for removing these effects were examined: 1) mechanically or chemically remove the offending specie from the propellant before the spectrum of propellant is made, and 2) make the IR spectrum of the whole propellant and then electronically subtract the spectrum of the offending specie from the spectrum of the whole propellant using the computer capability of the FTS-10.

Each technique had its advantages and disadvantages, these are discussed below.

Plasticizers

Ester-type plasticizers can be subtracted electronically from the spectrum of whole propellant. In order to accomplish this with a minimum perturbation to the propellant spectrum, a spectrum of the plasticizer must be made using the same ATR unit and IRE as used for the propellant. Use of the same ATR is important because of the pronounced spectral differences among spectra made with different ATR units and particularly the differences in spectra between ATR and transmission cells.

It was found that, if the ester peak at 1740 cm^{-1} is used for the subtraction, any propellant peak in the immediate vicinity of 1740 cm^{-1} is severely affected by the subtraction. Band width of the propellant peak changes and not all of the spectral influence of the plasticizer can be removed with 100% assurity. The reason for this is that the ester on the plasticizer is hydrogen bonded in propellant and a very slight wave number shift occurs in the ester peak as compared to the same peak in neat plasticizer.

If the peak at 1180 cm^{-1} (also ester group in the plasticizer) is used, the subtraction can be accomplished with some assurance that all of the spectral influence of the plasticizer has been removed. Also, this absorbance is characteristic of that part of the ester group which does not hydrogen bond, thus, there are no wave number shifts to contend with.

Even with subtraction on the basis of the 1180 cm^{-1} peak, the propellant spectral information at 1740 cm^{-1} is not quantitatively useful because of

the hydrogen bonding problem. If the 1740 cm^{-1} peaks are ignored in correlating peak changes with mechanical property changes, then the subtraction of plasticizer from whole propellant improves the general quality of the propellant spectra.

The spectrum of DOA and the spectrum of a propellant sol fraction containing DOA made in a transmission cell were examined using the computer program and the tabulated data. Peak wave numbers and amplitudes were checked to assure that there were no shifts in the location of spectral peaks. A spectrum of DOA is shown in Figure 31 and written above each major peak in the spectrum is the wave number location of that peak. Figure 32 contains the same information for the sol fraction of a propellant that contained DOA. An examination of the spectrum of DOA and the spectrum of the sol fraction reveals the presence of DOA and shows that the location of each of the DOA peaks to be the same in the two spectra.

There do not seem to be any obvious shifts in peak locations between the sol fraction and DOA. As has been noted, there is probably some hydrogen bonding to the carbonyl portion of the ester group in DOA which will result in a small shift in the shape of the DOA peak in the 1743 cm^{-1} region; and, in order to avoid the influence of hydrogen bonding on the subtraction, a peak located at 1180 cm^{-1} is preferable for accomplishing the subtraction.

Aluminum

Aluminum powder was found to create a upward drift in the baseline of the propellant spectra. The effect of subtracting the spectrum of aluminum from the spectrum of the various propellants was examined. Our principal concern was whether subtracting aluminum influenced the heights of the various peaks, particularly in the region 2000 to 600 cm^{-1}. The spectrum of aluminum used for these subtractions is given on Figure 33 and the effect of aluminum on the spectra of propellant can be seen by comparing Figure 34 with Figure 35. Figure 34 is the zero-aging-time propellant with AP removed and without subtraction of aluminum. Figure 35 is the same spectrum with the influence of aluminum subtracted. Heights of peaks at 965 cm^{-1} and 2920 cm^{-1} were ratioed for the spectra shown on Figures 34 and 35. The difference in the ratio of these two peaks between Figures 34 and 35 was a little less than 4%. If all spectra in a series are treated the same way and the same spectrum of aluminum subtracted from all of the aged propellant spectra, the influence of aluminum on the various propellant spectra can be ignored. However, this subtraction does apparently have some small influence on the magnitudes of the peaks.

General conclusions concerning subtraction of the spectral influence of aluminum from a spectrum of propellant are as follows.
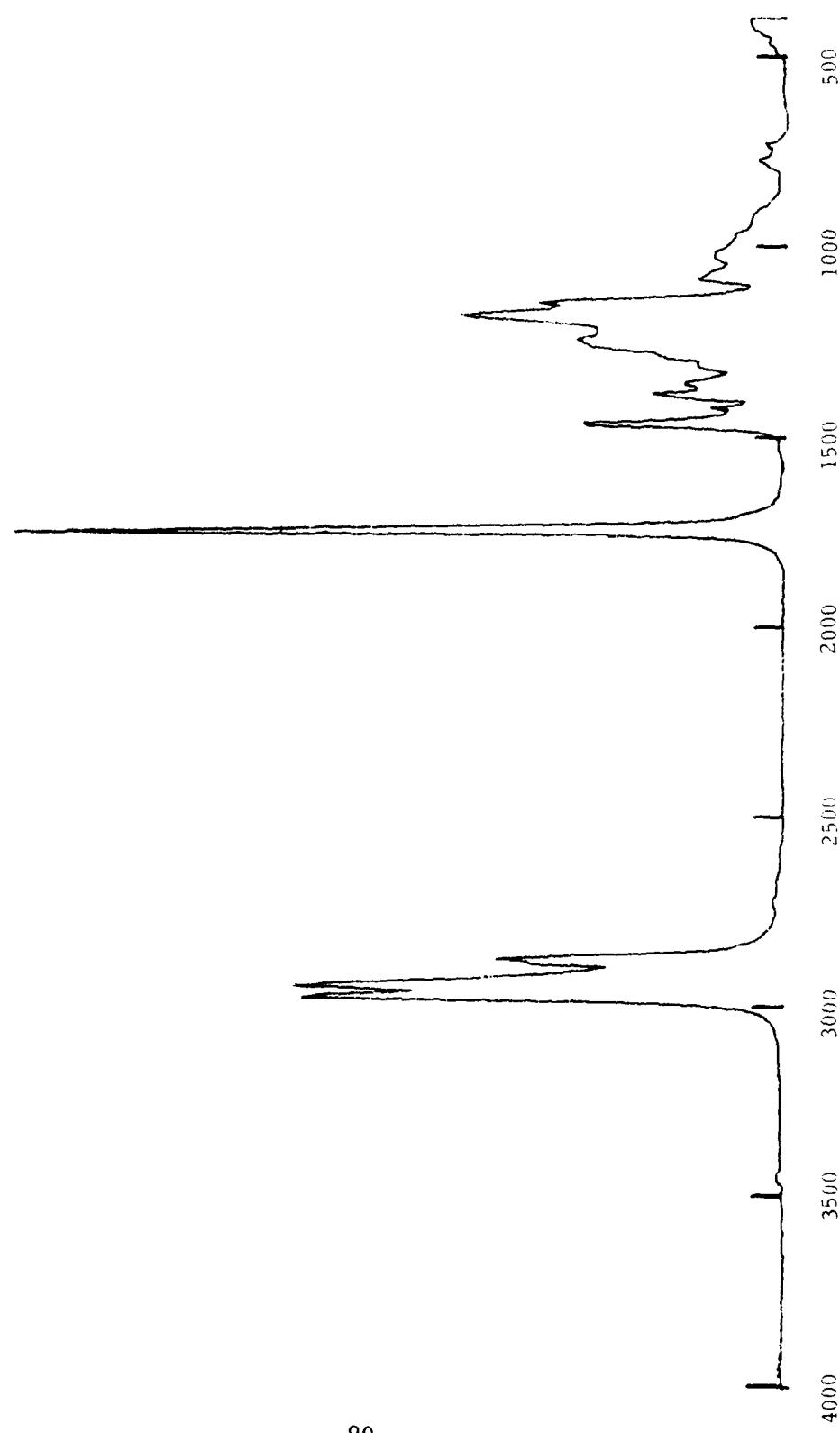
Figure 31. IR Spectrum of DOA

90
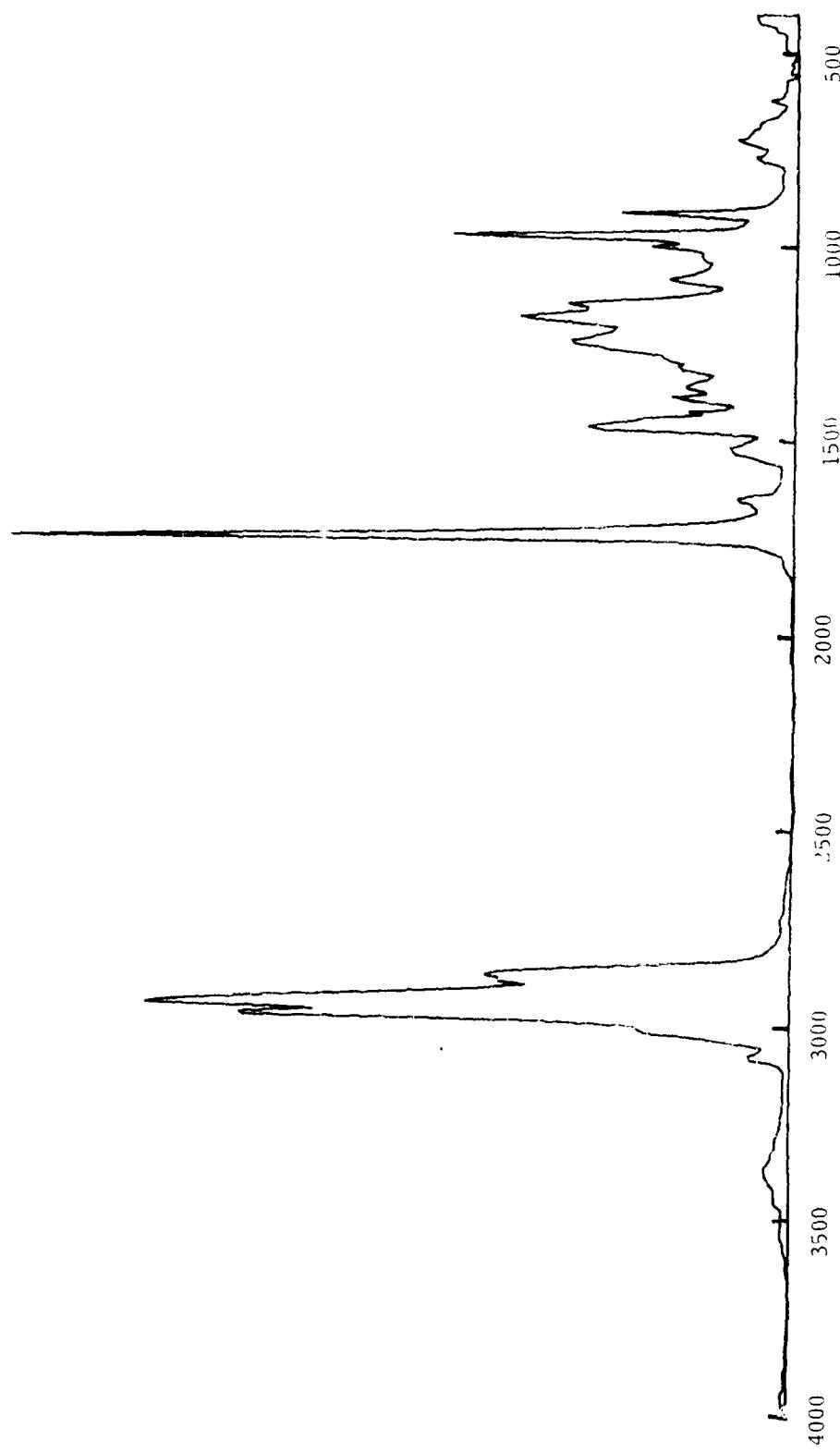
Figure 32. IR Spectrum of TP-H8259 Sol Fraction. Propellant Aged Zero Time

91
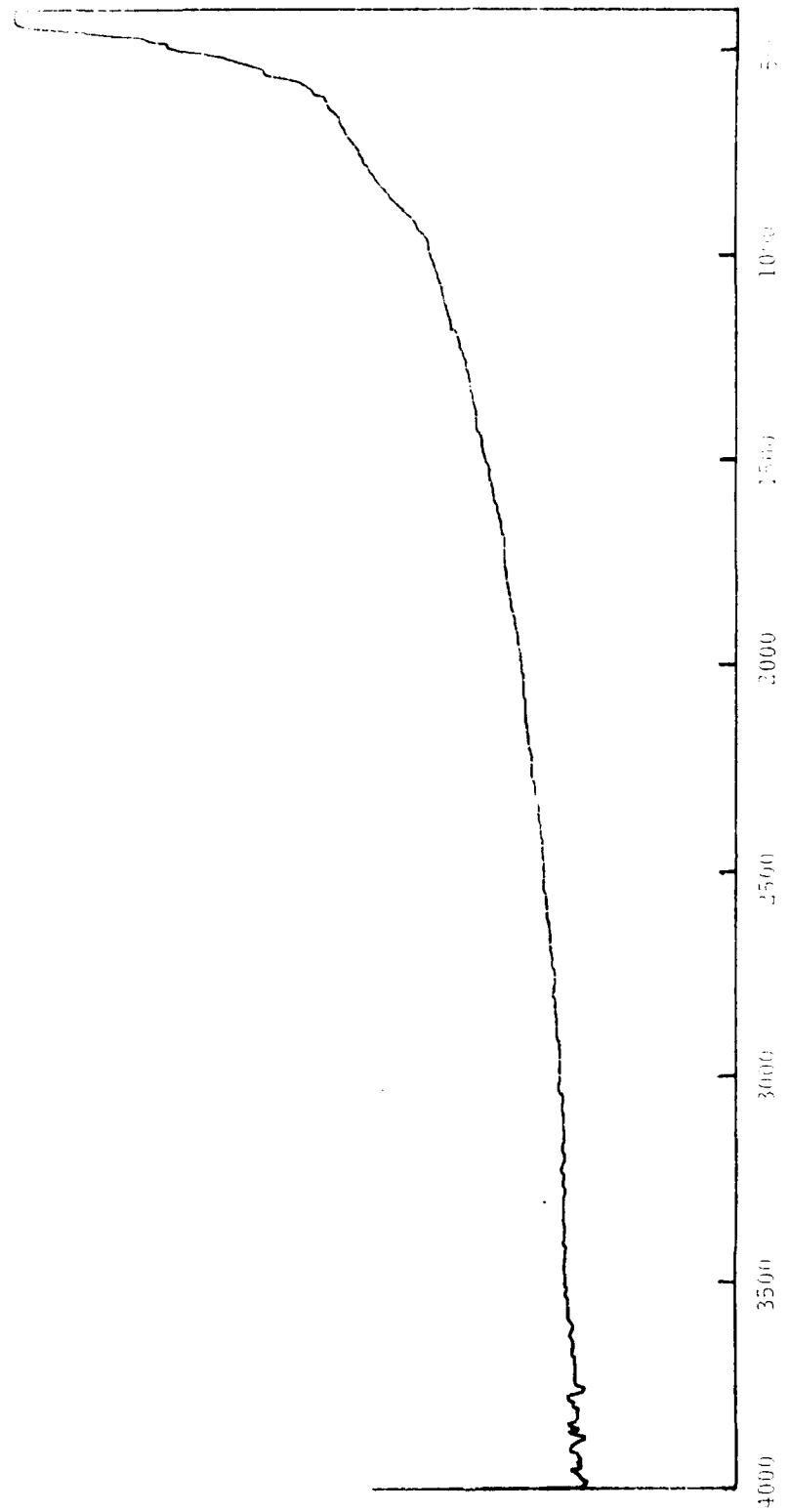
Figure 33. Infrared Spectrum of 30μ Aluminum Powder
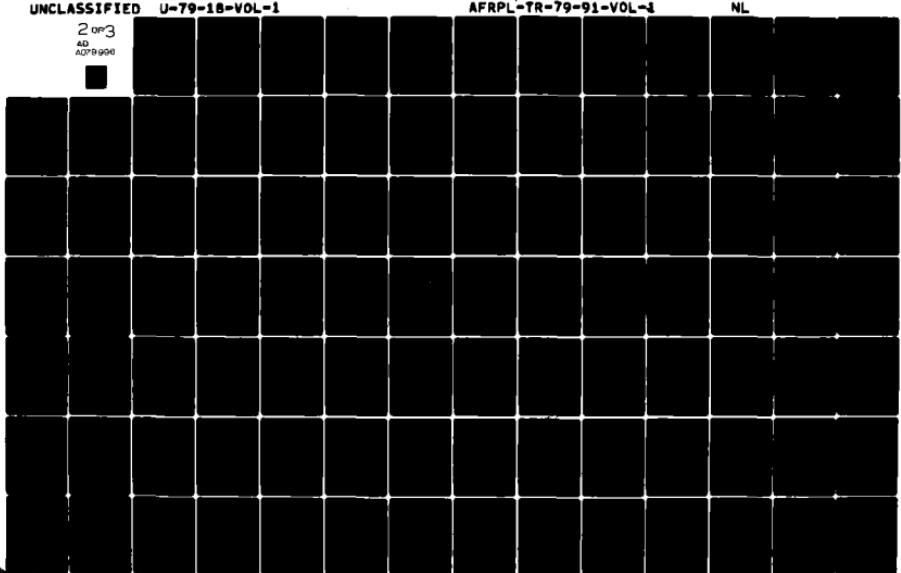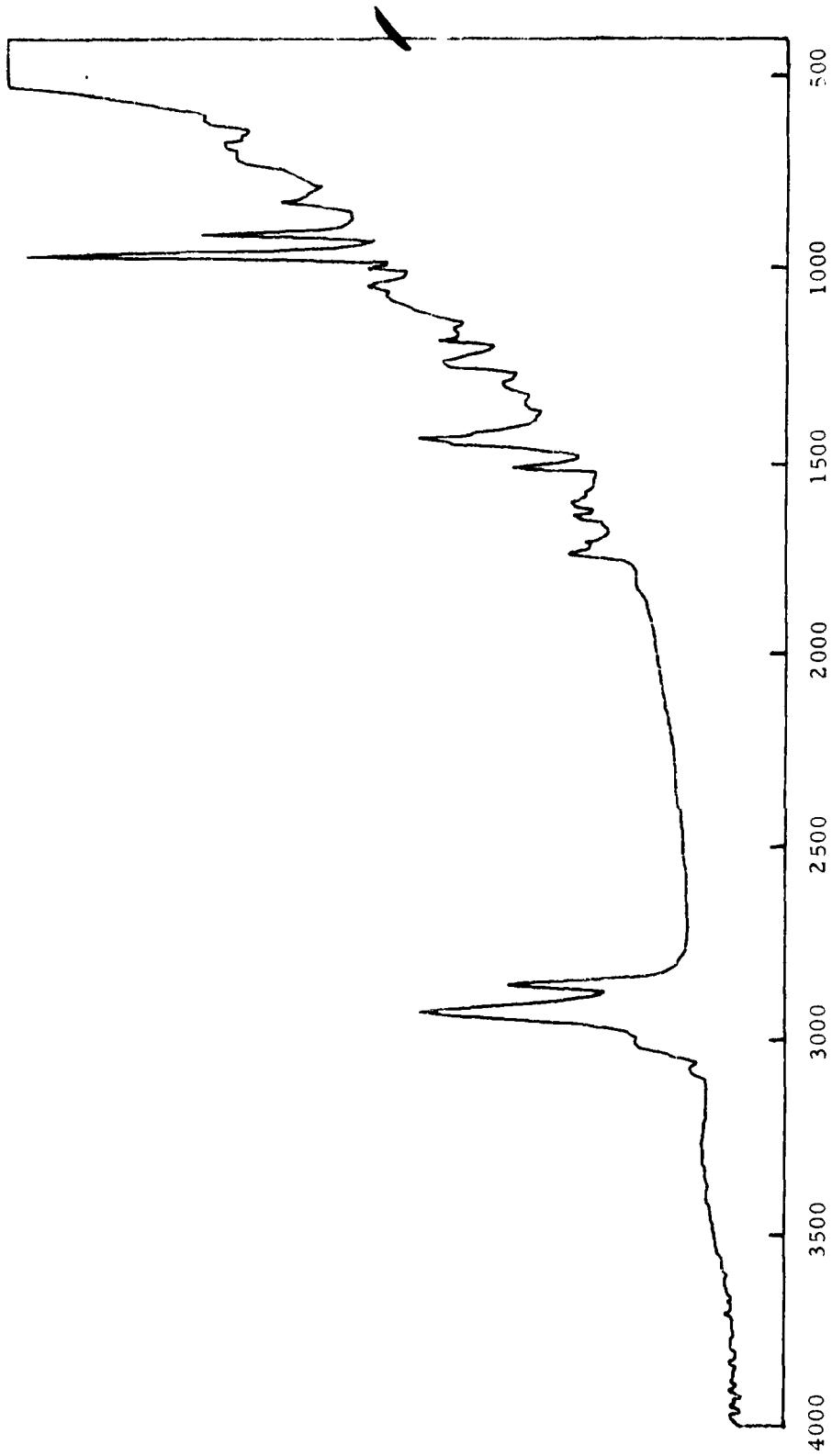
Figure 34. Infrared Spectrum of TP-H8156 at Zero Aging Time with AP Leached Out by Water.

93
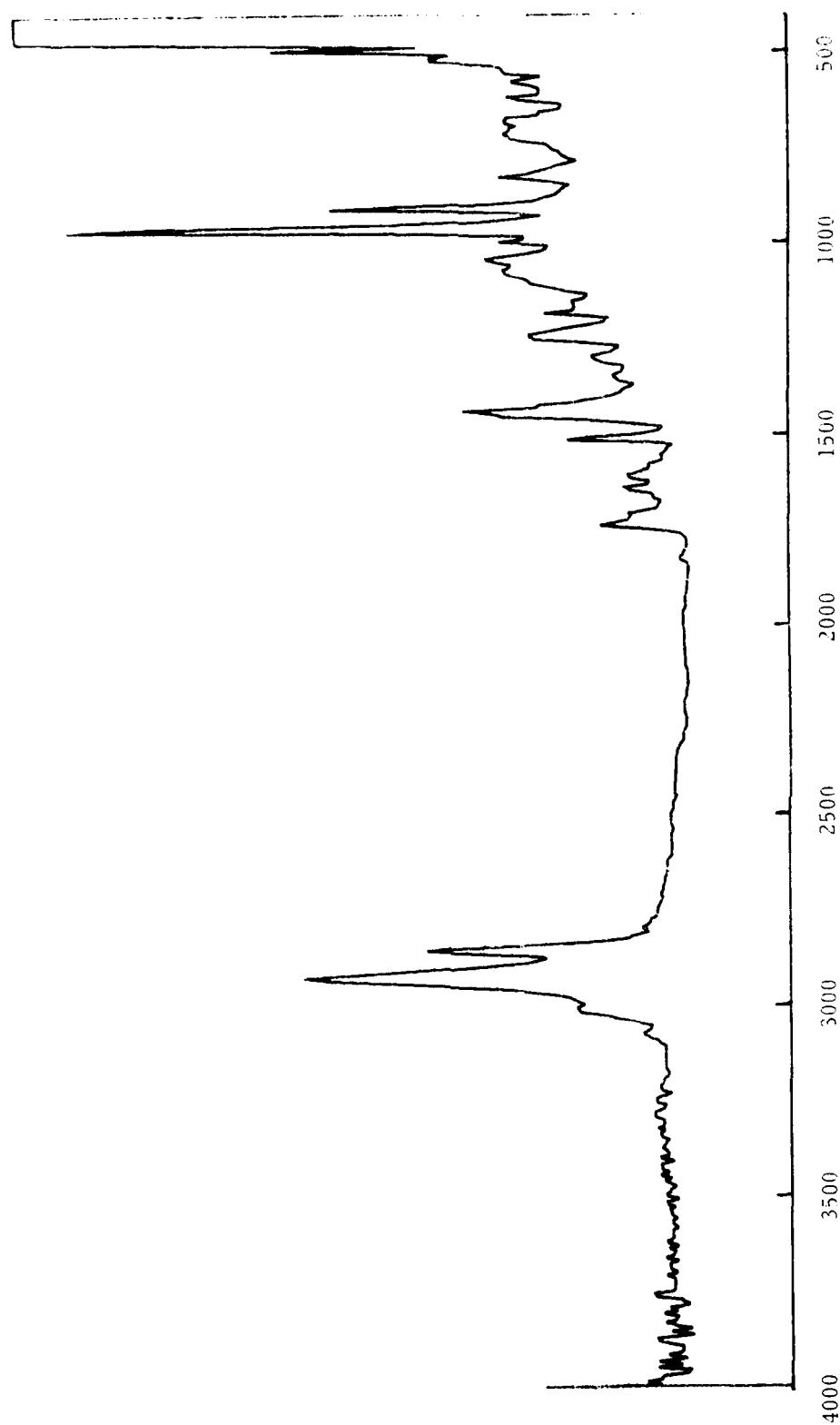
Figure 35. Infrared Spectrum of TP-H8156 at Zero Aging Time, AP Leached Out, and Aluminum Subtracted.

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1) It is easily accomplished.

2) It has little effect on the quantitative nature of the propellant spectrum.

3) It makes the propellant spectrum look nice.

4) Al does not strongly influence propellant spectra and, thus, usually there is no need to subtract it.

Ammonium Perchlorate - By Subtraction

The spectrum of ammonium perchlorate taken by an ATR technique is changed depending upon the particle size of the ammonium perchlorate. Once this fact was established, the problem became one of how to deal with these changes and create a spectrum of ammonium perchlorate that could be used to subtract its spectral influence from the spectrum of whole propellant. Any of a number of spectra of ammonium perchlorate can be used in the subtraction, but the quantitative utility of the resulting propellant spectrum is highly questionable.

The problem centers about two peaks, one occurring in the vicinity of 1420 cm^{-1} and the other peak occurring at approximately 1045 cm^{-1}. The peak at 1420 cm^{-1} is the least troublesome. Its shape and the wave number location do not shift appreciably with particle size. The peak occurring at approximately 1045 cm^{-1} is the most troublesome, because it broadens as the particle size of the ammonium perchlorate is increased and because the location of the spectral peak shifts from approximately 1045 cm^{-1} downward to approximately 1020 cm^{-1} as ammonium perchlorate particle size is increased.

Two other features in the spectra of ammonium perchlorate are subject to this same shift, but not to as great an extent. These are the peaks occurring in the vicinity of 3270 cm^{-1} and 620 cm^{-1}. Because there is not much useful in the propellant binder at either of these locations, the shifts that occur in the spectra of the AP are not of major concern. Our efforts were directed to identifying methods by which the peak shape and peak location in the 1020 to 1045 cm^{-1} region can be adjusted so that the spectrum of ammonium perchlorate shows the peak shape, at this location, in whole propellant.

Using our computer program to reduce the spectral data and give us precise amplitude and wave number locations of peaks in ammonium perchlorate, we were able to identify the shifts that were taking place in 16 μ and ammonium perchlorate. These two spectra are shown on Figures 36 and respectively.

To illustrate the problem, examine the spectrum displayed on Figure 38. This is propellant taken at "0" aging time and with the spectral influence of
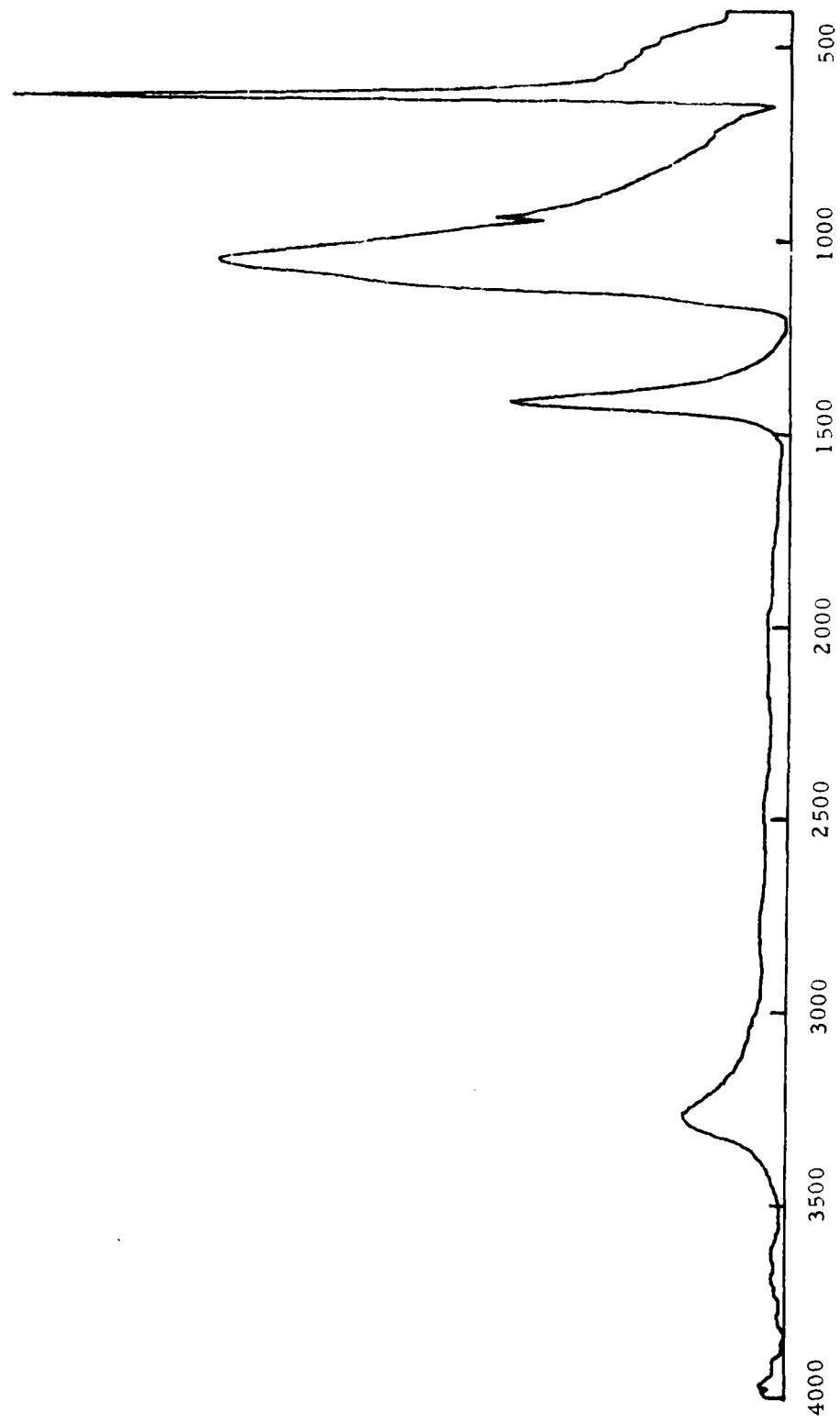
Figure 36.   IR Spectrum of 16μ AP
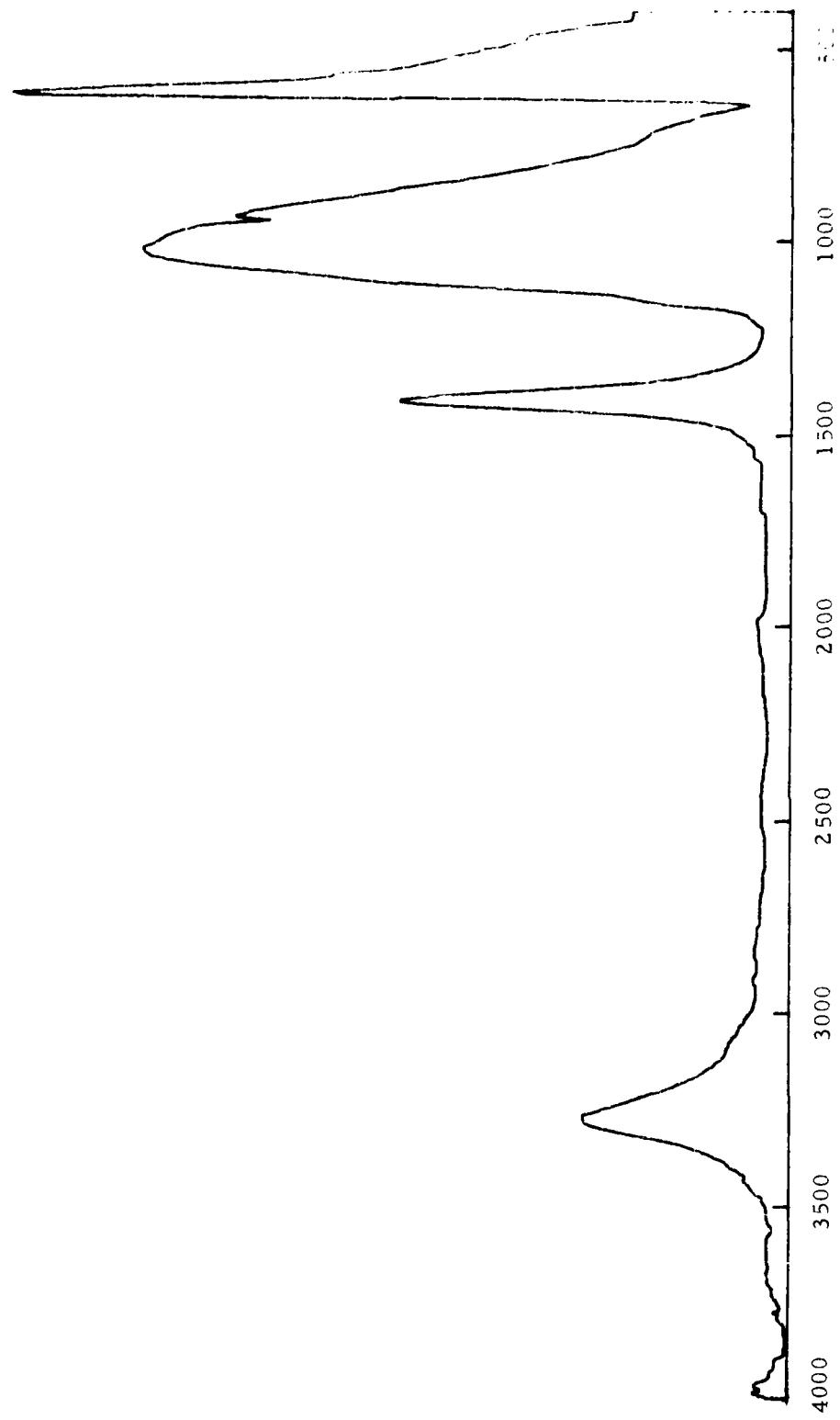
Figure 37. IR Spectrum of 200 μ AP
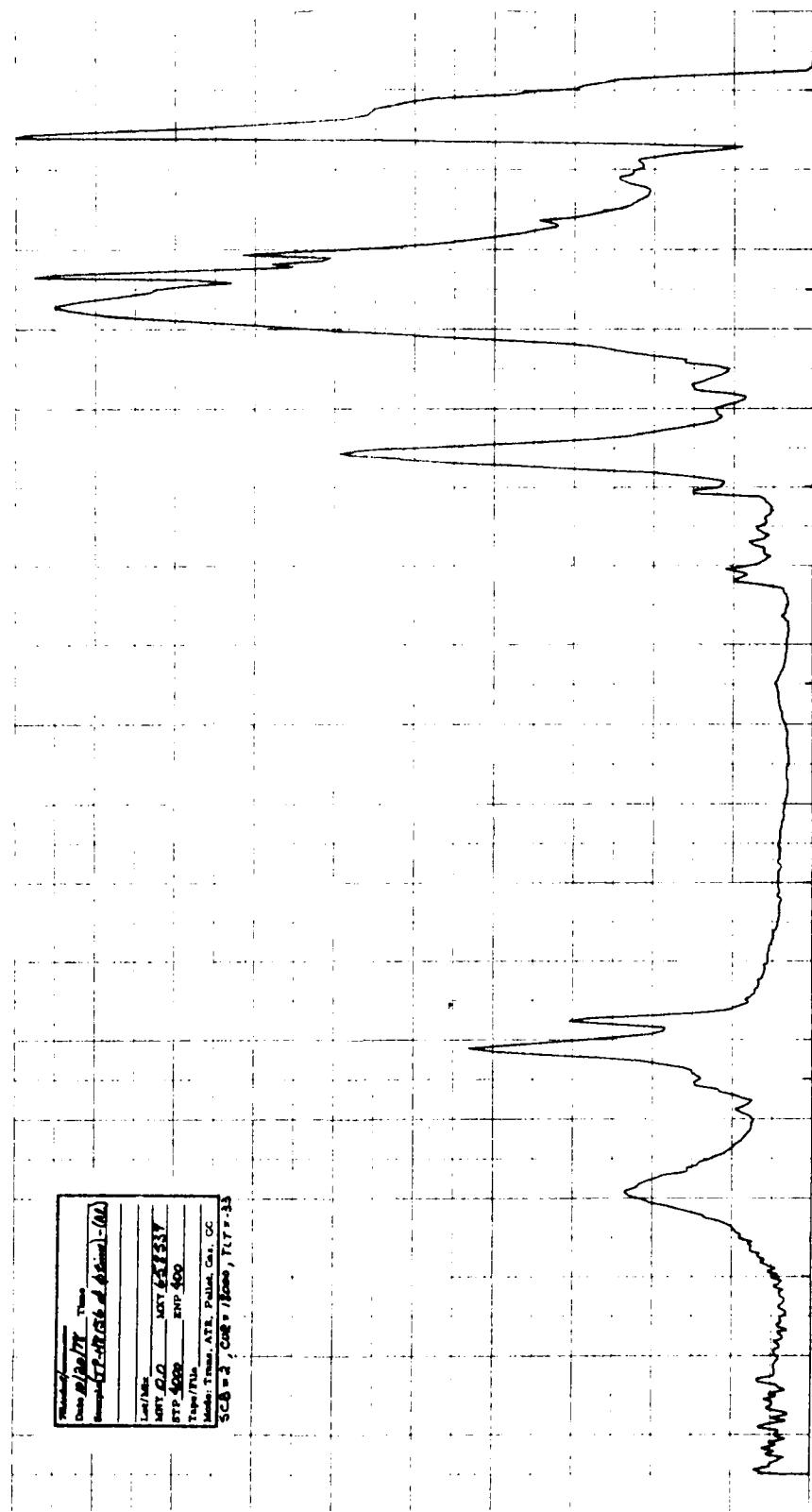
Figure 38. IR Spectrum of TP-H8156 at Zero Aging Time, Al Subtracted

aluminum subtracted so that the upward baseline drift has been removed. Note that the peak appearing at about 1045 cm^{-1} has a shape that falls somewhere between the shape of the same peak in the 16 μ and 200 μ ammonium perchlorate. The location of the peak is near the same point as in the 16 μ AP, but, in actuality, when one examines the reduced data, it is shown that the location of the peak in propellant is one data point different from the location of that same peak in the 16 μ AP. It is obvious, looking at Figure 37, that the location of this peak in propellant is vastly different from the location of the peak in the 200 μ AP, yet the width of the peak in propellant resembles somewhat the width of the peak in the 200 AP.

A spectrum of ammonium perchlorate was synthesized using the spectra of 16 μ and 200 μ AP. These two spectra were added together in the proportions that would locate the apex of the 1040 cm^{-1} peak at the point where it lies in the spectrum of whole propellant. Not only did this place the apex of the peak in the correct spectral position, but it also altered the shape of the peak such that it very closely resembled the shape of the peak found in propellant. This synthesized spectrum of ammonium perchlorate is shown in Figure 39.

This synthesized spectrum of ammonium perchlorate was subtracted from the spectrum of whole propellant at a variety of scaling values. These spectra and their scaling factors (SCB) are all shown on Figure 40. The final scaling factor (where SCB = 1.646) reduced the peaks at 1040 cm^{-1} and 1420 cm^{-1} to near zero contribution to the spectrum of propellant. However, this was probably too large a scaling factor because there is a sharp negative peak in the vicinity of 1120 cm^{-1} ... a feature that does not show in the spectrum of propellant from which the ammonium perchlorate had been leached. A review of the spectra displayed on Figure 40 shows that the spectrum where SCB = 1.25 is more like the spectrum of propellant from which ammonium perchlorate had been leached by water, than any of the other spectra on Figure 40. A plot of the spectrum, where SCB = 1.25, is given on Figure 41.

This technique yielded the best AP subtraction in the program and was encouraged to believe that it may be possible to subtract ammonium perchlorate from the spectrum of whole propellant and have the data quantitatively usable. There are still some problems to be resolved; primarily to establish a set of "rules" for determining when the proper amount of ammonium perchlorate has been subtracted. Until such "rules" are established, it is best not to try to subtract AP from a spectrum of whole propellant, for to do so would always raise some doubt as to the validity of the resulting propellant spectrum.

Ammonium Perchlorate - By Leaching

A second possibility for removing the spectral influences of AP from spectrum of whole propellant was investigated ... washing or leaching AP
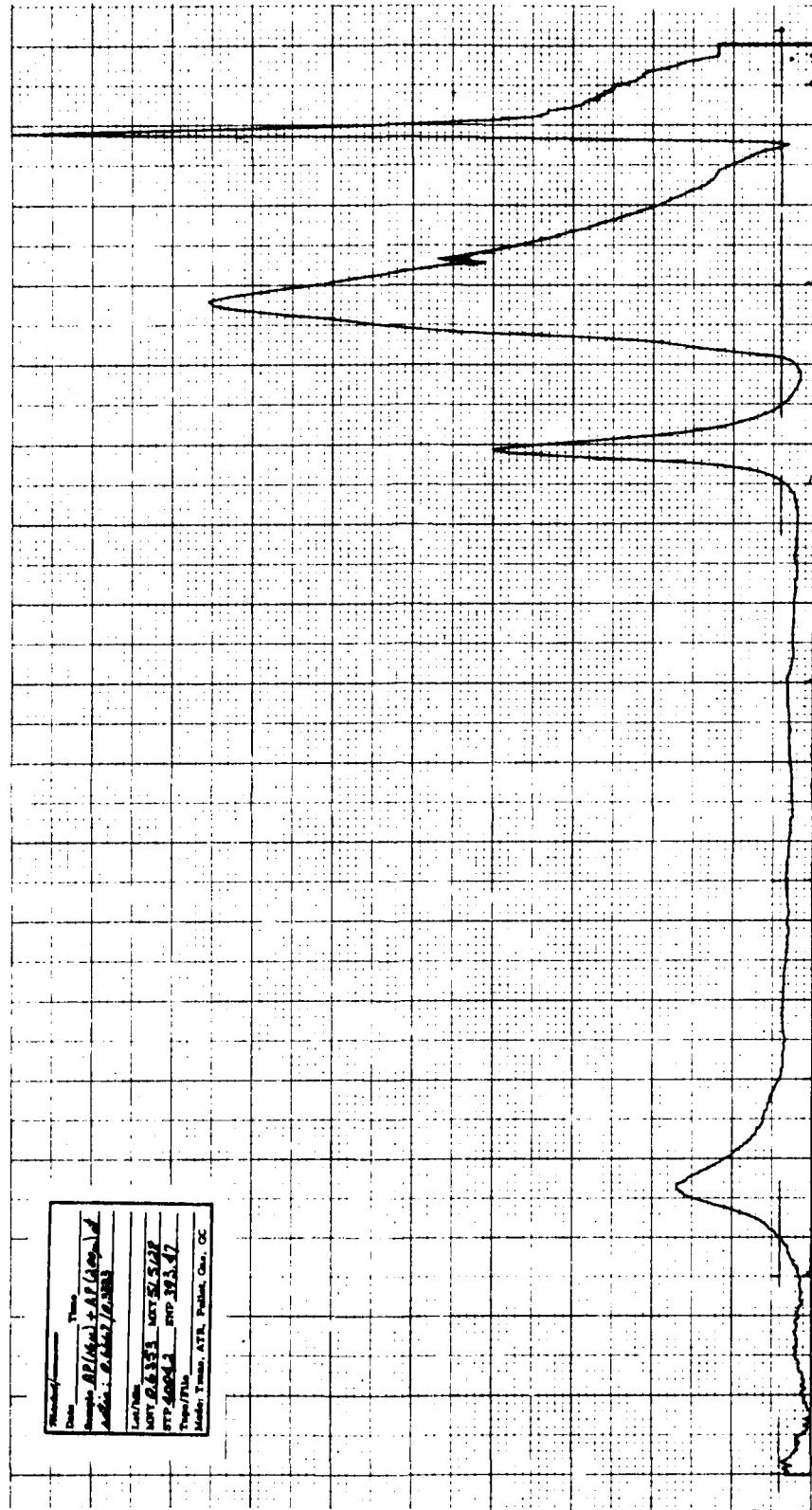
Figure 39. IR Spectrum of 16μ AP + 200μ AP at 0.6667/0.3333 Ratio
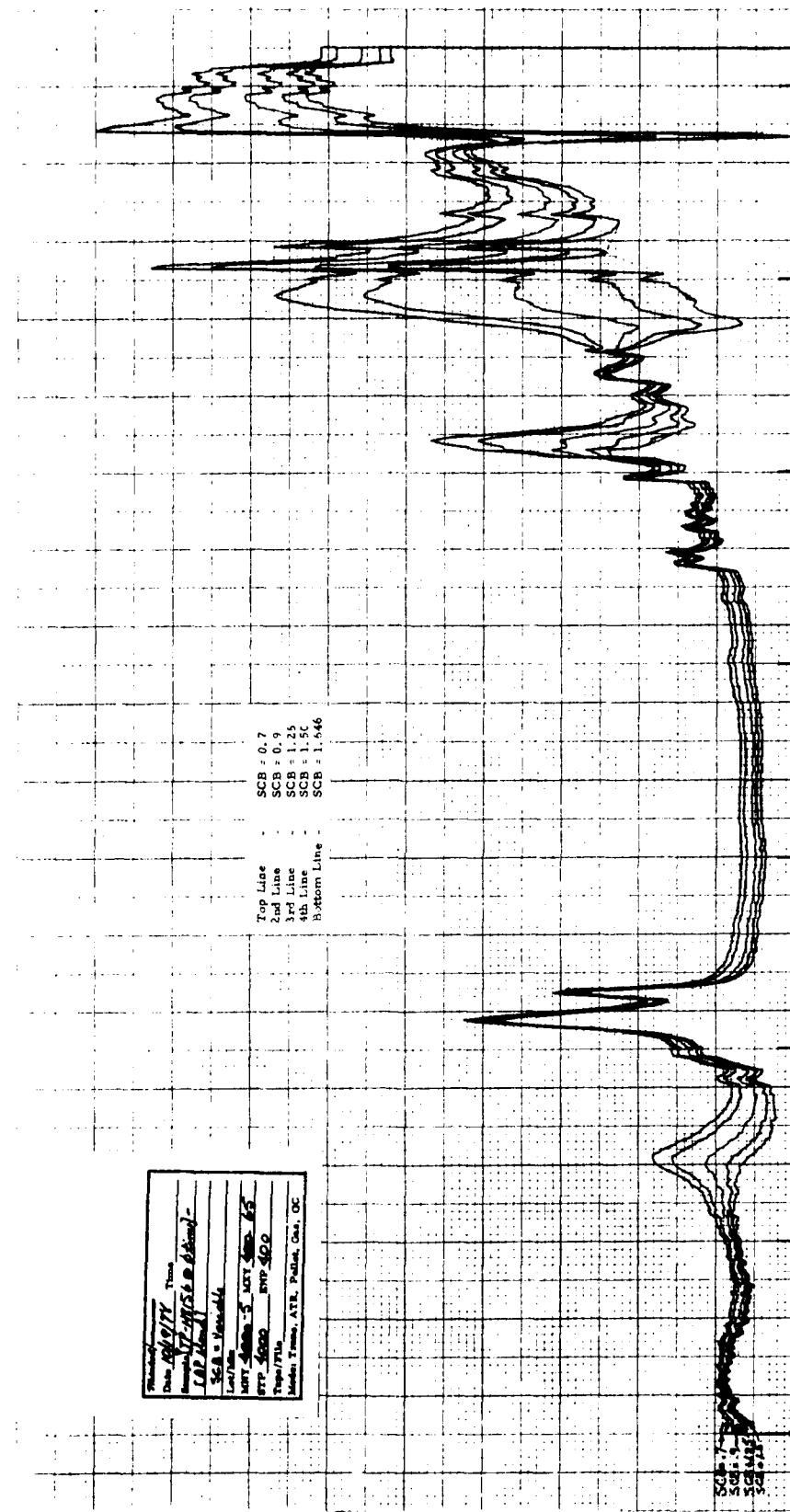
Figure 40. Subtraction of AP Blend (Figure 39) From TP-H8156 (Figure 38) at Various Scaling Factors

101
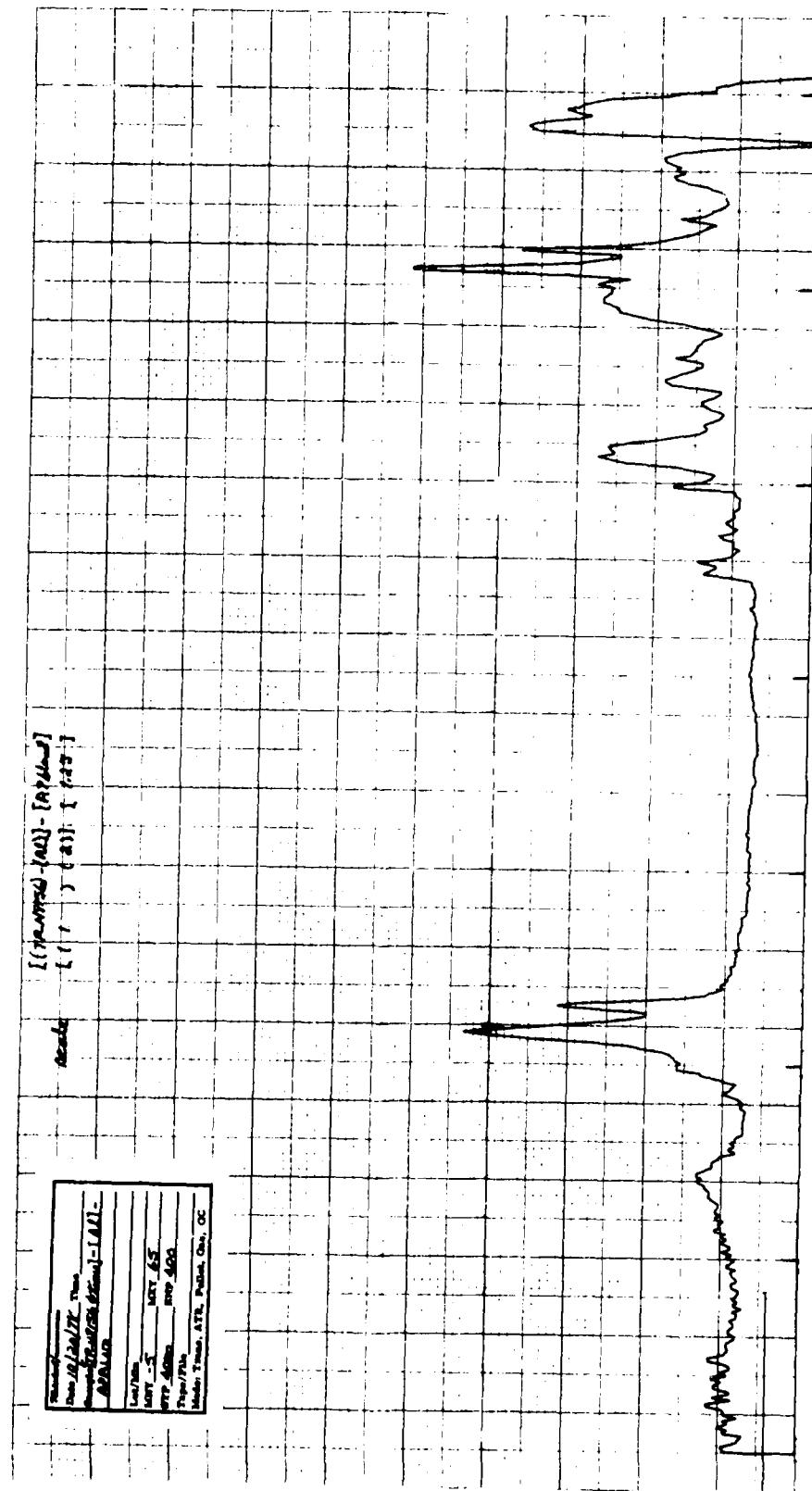
Figure 41. TP-H8156 at Zero Aging Time Minus A1 and AP (Where SCB = 1.25)

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... the propellant with warm water. In order to test the technique, samples
... TP-H8156 propellant aged at six temperatures for 12 months were washed
... move the AP; and the IR spectra of these washed samples were made.
... the whole propellant were compared to these washed samples and
... ation made of the benefits accrued by leaching AP from propellant.

Experiment A - Ammonium perchlorate was leached from several
... of TP-H8156 propellant samples. These samples had been aged
... months at 75°, 110°, 130°, 150°, 170°, and $190^\circ F$. The ammonium
... chlorate leaching procedure was to submerge all samples from a particu-
... temperature in a trough of running water at 35° to $40^\circ C$ for periods
... to 24 hours or until the ammonium perchlorate had been removed.
... samples were then dried in an oven at 55° to $60^\circ C$ for 4 hours and
... night at room temperature. Infrared spectra of all propellant
... 43 samples, were run.

Experiment B - The infrared data accumulated on each of the unleached
... used in "A" above were accumulated and reduced by the computer.
... spectra were the ones originally run at the time that the samples
... inally tested; i.e., for the "0" time spectrum, a one-year old
... was used, for the one-month aging samples, 11-month old spectral
... used, so that the spectra employed in this experiment were the
... nes.

... data from these two experiments are presented in Appendix E.
... data and conclusions are presented here.

... shows the correlations among peak height changes and mechani-
... changes for the leached and unleached propellant. Some very
... correlations were found to exist if the spectra of propellant aged
... at various temperatures were combined and correlated with pro-
... mechanical properties. Plots of these correlations are given in
... through 48.

... clusions concerning these experiments are as follows:

... We know that leaching ammonium perchlorate from propellant
... some organic material from the propellant in addition to removing
... ammonium perchlorate. Although this makes the organic portion of the
... spectrum more visible, it does change the nature of the correla-
... are found between peak height changes and mechanical property
...

TABLE 15

CORRELATIONS FOUND FOR LEACHED & UNLEACHED TP-H8156

WAVE NO. CORRELATING WITH MECHANICAL PROPERTIES AT AGING CONDITIONS

WAVE No.	190°	170°	150°	130°	110°	75°	12 Mths.
Whole Propellant							
1744				σ			
1713	E	E			E	E	E
1515	ε	ε					σ ε
1250	ε	ε	ε				σ ε
AP Leached Prop.							
1738	E	E σ					ε E
1437							σ
1244	σ						
912	ε	ε		ε	ε		ε E

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Aged 12 months at various temperatures.

Peak Height Correlations with Mechanical Properties

Relative Peak Height

AGED 12 MONTHS AT
VARIOUS TEMPERA-
TURES

SPECTRA NORMALIZ-
ED AT 2920 cm^{-1}

Figure 43.   Relationship of Spectral Peak Height Changes to
Propellant Mechanical Properties

AGED 12 MONTHS AT
VARIOUS TEMPERATURES

SPECTRA NORMALIZED
AT 2920 cm^{-1}

Figure 44.   Relationship of Spectral Peak Height Changes to
Propellant Mechanical Properties

AGED 12 MONTHS AT VARIOUS
TEMPERATURES

SPECTRA NORMALIZED AT
2920 cm^{-1}

Figure 45. Relationship of Spectral Peak Height Changes to
Propellant Mechanical Properties

TP-H8156/V6-13 Aged 12 mo. at various temp.
AP leached from propellant
Normalized at 2920 cm^{-1}
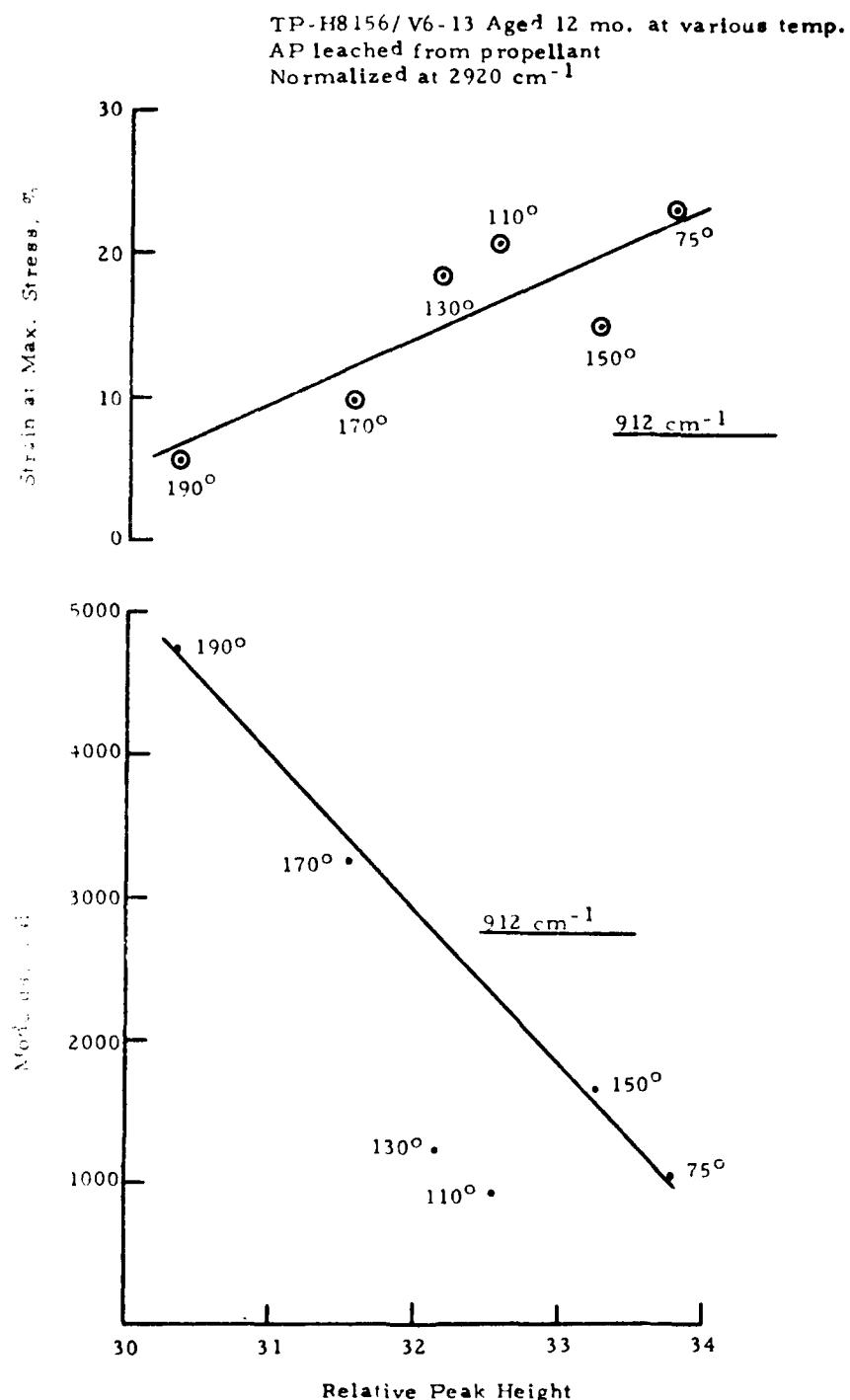
Figure 46.   Correlation of Peak at 912 cm^{-1}, Modulus and Strain.
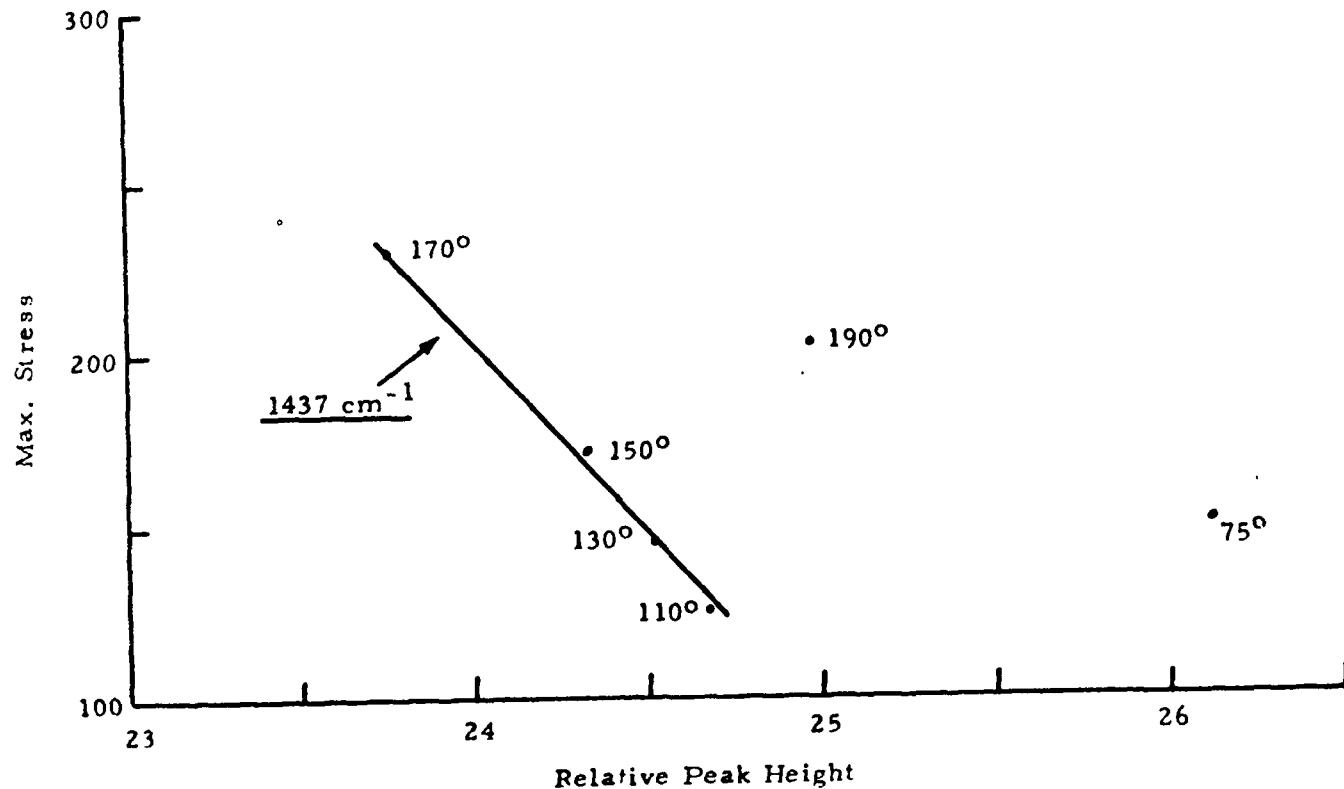
Figure 47. Correlation of Peak at 1437 cm^{-1} and Maximum Stress

TP-HF156/V6-13 aged 12 mo. at various temp.
AP leached from propellant
Normalized at 2920 cm^{-1}
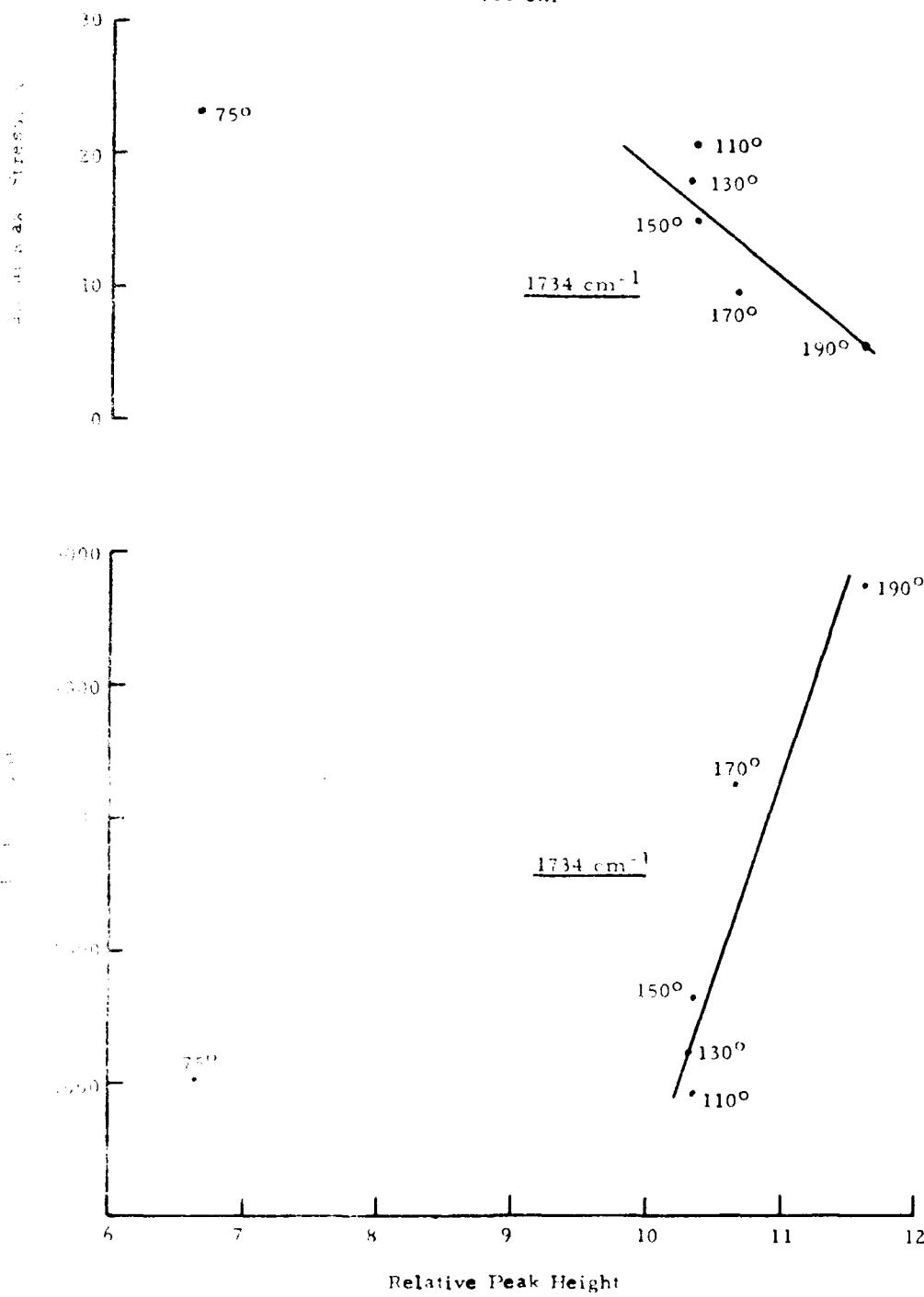
Figure 48. Correlation of Peak at 1734 cm^{-1}, Modulus and Strain.

2) Propellant from which ammonium perchlorate has been leached does have valid correlations between peak height changes and propellant mechanical properties.

3) Leaching ammonium perchlorate from propellant adds a step in the analysis of the propellant which may not be necessary. Certainly, for the propellant that we examined in this series, that step would not be necessary. For other propellant formulations, it may be a very necessary step.

4) Valid correlations are found with whole propellant in spite of the spectral influence of ammonium perchlorate. In fact, more correlations were identified with whole propellant than with propellant from which ammonium perchlorate had been leached.

5) Correlating spectral changes where time is a constant and aging temperature is the variable provides valid correlations. Here the mechanical properties of a propellant can be identified from a plot of spectral peak height changes versus mechanical property.

6) The case described in conclusion 5 will permit us to take a piece of propellant, regardless of how it has been aged and determine its mechanical properties merely by analyzing its infrared spectrum. This would be particularly important in determining the mechanical properties of a rocket motor aged in the field where aging conditions are unknown.

Evaluation of Binder Separated from Propellant

Two new techniques for acquiring the infrared data on aged propellant were investigated. These techniques were: 1) examine the sol fraction of propellant, and 2) examine the AP-leached gel fraction of propellant. With the addition of these two techniques for acquiring the IR data, there are procedures, all with the same propellant, TP-H8278, from Mix W-65:

1) IR spectrum of whole propellant.

2) IR spectrum of ammonium perchlorate-leached propellant.

3) The propellant sol fraction.

4) AP-leached gel fraction.

These four techniques were applied to samples of TP-H8278/W-65 that had been aged 0 to 16 weeks at 165°F. The results of the analysis of the IR data from these four methods are discussed below in Appendix G. Since this part of this report pertains to the effects of using propellant sol and gel fractions only, the discussions of whole propellant and AP-leached propellant are in Appendix G.

Sol Fractions

Infrared spectra used for this statistical analysis were obtained from the Aged Binder project aging program. Statistical analysis of these data was performed as a part of the FTIS project. A typical spectrum of the sol fraction of TP-H8278, Mix W-65 is displayed on Figure 49. This particular sample of propellant aged 1.4 weeks at 165°F.

Reduction of these sol spectra was performed using the peak at 2840 for normalizing with a minimum-to-tangent baseline as illustrated in Figure 49. The large trans peak and small vinyl peak in the 950 to 1000 cm^{-1} range were tested with a common baseline. These data were reduced prior to finding that the common baseline routine allowed for measuring the normalizing peak from a common baseline; however, a check with the hand reduction method used in the LCB program (to establish the percent cis, trans, and vinyl unsaturation) showed that the relative quantities of all materials were extremely close as measured by the computer with its minimum-to-tangent baseline for the normalizing peak and the common baseline technique as used in the LCB program for measuring the normalizing peak at 2840 cm^{-1}. Figure 49 shows the location of the baseline used in the LCB program for hand data reduction to establish the percent of cis, trans, and vinyl unsaturation.

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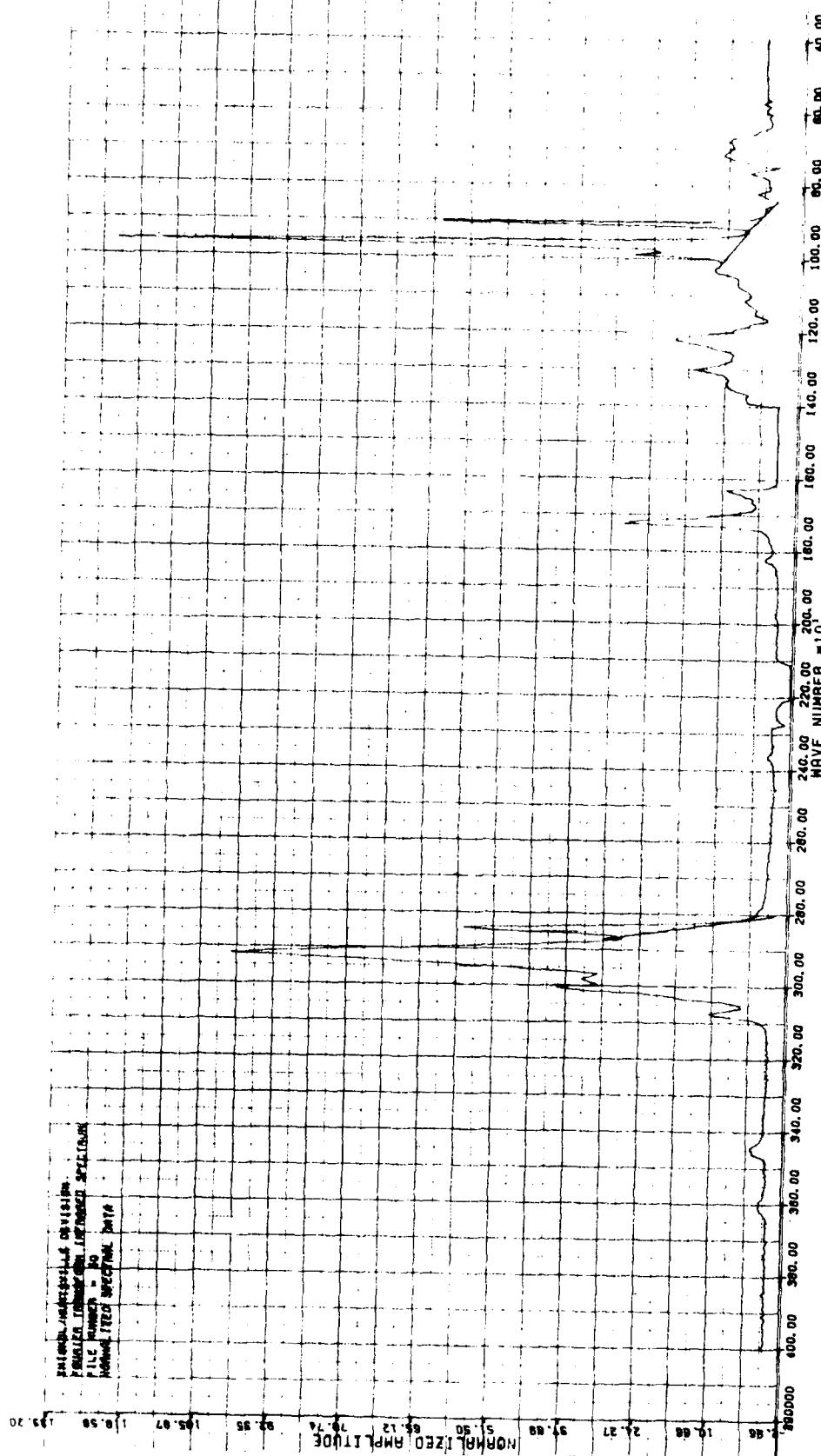
Figure 49. Typical IR Spectrum of TP-H8278/W-65 Sol Fraction (Propellant Aged 1.4 Weeks at 165°F). Minimum-to-Tangent Baseline for Normalizing Peak (2840 cm^{-1}).

114
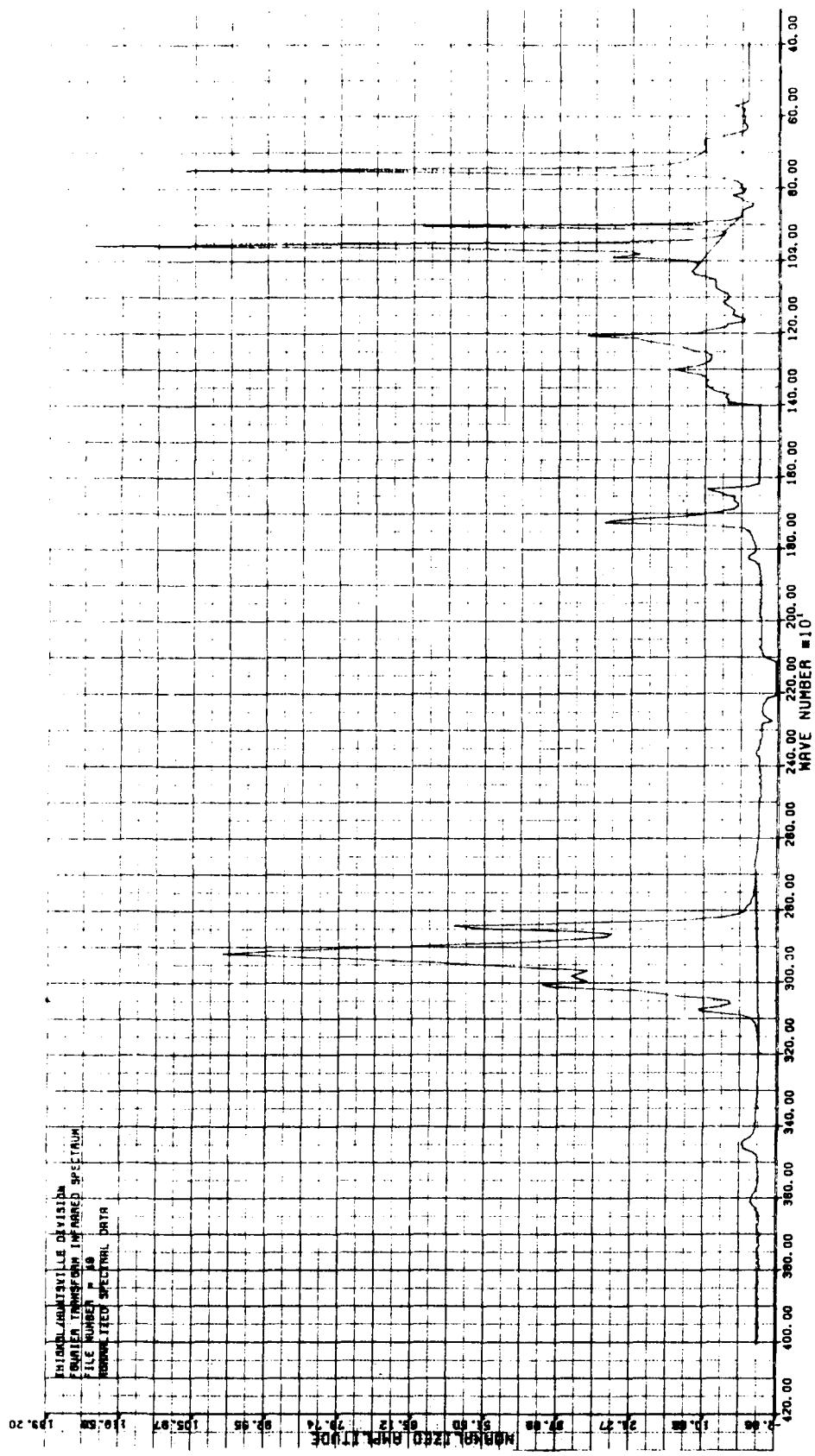
Figure 50. Typical IR Spectrum of TP-H8278/W-65 Sol Fraction (Propellant Aged 1.4 Weeks at 165°F). Common Baseline for Normalizing Peak (2840 cm^{-1}).

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After the infrared data were reduced by computer the height of various peaks at each of the time intervals and the mechanical properties of the propellant at the corresponding time intervals were combined and run in a statistical analysis program. Each test time was replicated giving a total of 18 observations for the statistical analysis. Simple correlations are displayed in Table 16 and show that four peaks correlated with at least one of the propellant's mechanical properties. Based upon 18 observations a correlation coefficient of at least 0.59 is required for the 99% confidence level. All of the correlation coefficients displayed in Table 16 are greater than this value.

Multiple correlations were also calculated for each of the three mechanical properties... modulus, stress, and strain. The number of peaks included in the equation for each mechanical property was different in each instance. Table 17 is a listing of the multiple correlation information found for modulus. This equation contains five terms and resulted in a correlation coefficient of 0.9473. With 18 observations and 13 degrees of freedom, the correlation coefficient required for a 99% confidence level is 0.785 and the correlation coefficient for modulus exceeds this value by a large amount. It is also interesting to note that using this equation the standard error of estimate was reduced by approximately 2/3 over the standard error of estimate of the raw modulus data.

Multiple correlation equations for the parameters stress and strain are presented in Tables 18 and 19, respectively. Both of these equations have a correlation coefficient that indicates that the confidence level is in excess of 99%. The equation for stress appears to be particularly good in that the standard error of estimate going into the statistical analysis was 20.3; and, with the equation applied, the standard error of estimate was reduced to 6.02 psi.

The equation for strain is not quite as good as the other two; but, on the other hand, measurement for strain for this propellant seems to have a large amount of variability in it; however, the equation for strain (on Table 19) does show a reduction in the standard error of estimate by about 50%.

The three correlation equations are shown graphically on Figures 51, 52, and 53. These figures are plots of calculated value against measured value with the individual data points displayed about the 100% correlation line. Since all of the data points represent duplicates, it is interesting to note how closely the duplicates correspond with each other; for the sol fractions replication of data is reasonably good.

It was noted earlier that an infrared technique had been used during the LCB program to determine the amount of cis, trans, and vinyl unsaturation remaining in the propellant's binder after aging for particular lengths of time. Table 20 is a tabulation of the quantity of each of the types of unsaturation remaining in the propellant after aging at two temperatures for a variety of time periods. The quantity of trans unsaturation and vinyl unsaturation have been plotted against maximum stress and modulus to determine whether there might be a correlation between the absolute quantity of unsaturation and these two propellant mechanical properties. These plots are shown on Figures 54 and 55, and each data point shown is the average of two determinations of

TABLE 16

SIMPLE CORRELATIONS OF PEAK HEIGHT CHANGES

AND MECHANICAL PROPERTY CHANGES

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, Sol Fraction)

| | Correlation Coefficient for Mechanical Properties | | |
Peak, cm^{-1}	Modulus	Stress	Strain
2919	0.7338	0.9229	
1300	-0.6171		
960	-0.6752	-0.7186	
820			0.7122

For 18 observations (9 test times x 2 replicates): $r_{.99} = 0.590$

TABLE 17

MULTIPLE CORRELATION FOR PEAK HEIGHT

CHANGES AND MODULUS

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, Sol Fractions)

MODULUS = 5581 - 395.1(X_2) + 56.28 (X_4) - 23.28 (X_9) - 241.5 (X_{11})

Where: X_2 = height of peak at 3004 cm^{-1}

X_4 = height of peak at 2919 cm^{-1}

X_9 = height of peak at 960 cm^{-1}

X_{11} = height of peak at 820 cm^{-1}

R = 0.9473

R^2 = 0.8974

Standard Error of Estimate Going In = 342.7 psi

Standard Error of Estimate w/Equation = 125.6 psi

For 18 observations and 13 degrees of freedom: $R_{.99} = 0.785$

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TABLE 18

MULTIPLE CORRELATIONS FOR PEAK HEIGHT

CHANGES AND STRESS

(TP-H8278/W-65, Aged 0 to 16 Wk at 165°F, Sol Fractions)

STRESS = -133.6 + 6.854 (X_4) -6.104 (X_6) -1.347 (X_9)

Where: X_4 = height of peak at 2919 cm^{-1}

X_6 = height of peak at 1633 cm^{-1}

X_9 = height of peak at 960 cm^{-1}

R = 0.9649

R^2 = 0.9310

Standard Error of Estimate Going In = 20.83 psi

Standard Error of Estimate w/Equation = 6.02 psi

For 18 observations and 14 degrees of freedom: $R_{.99}$ = 0.737

TABLE 19

MULTIPLE CORRELATION FOR PEAK HEIGHT

CHANGES AND STRAIN

(TP-H8278/W-65, Aged 0 to 16 Wk at 165°F, Sol Fractions)

STRAIN = -28.43 + 3.562 (X_2) + 1.682 (X_{11})

Where: X_2 = height of peak at 3004 cm^{-1}

X_{11} = height of peak at 820 cm^{-1}

R = 0.8495

R^2 = 0.7217

Standard Error of Estimate Going In = 1.609% Strain

Standard Error of Estimate w/Equation = 0.904% Strain

For 18 observations and 15 degrees of freedom: $R_{.99}$ = 0.677

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TP-H8278/W-65
Aged 0 to 16 Wks at 165°F
Sol Fractions

R = 0.9473

$R^2 = 0.8974$

$R_{.99} = 0.785$
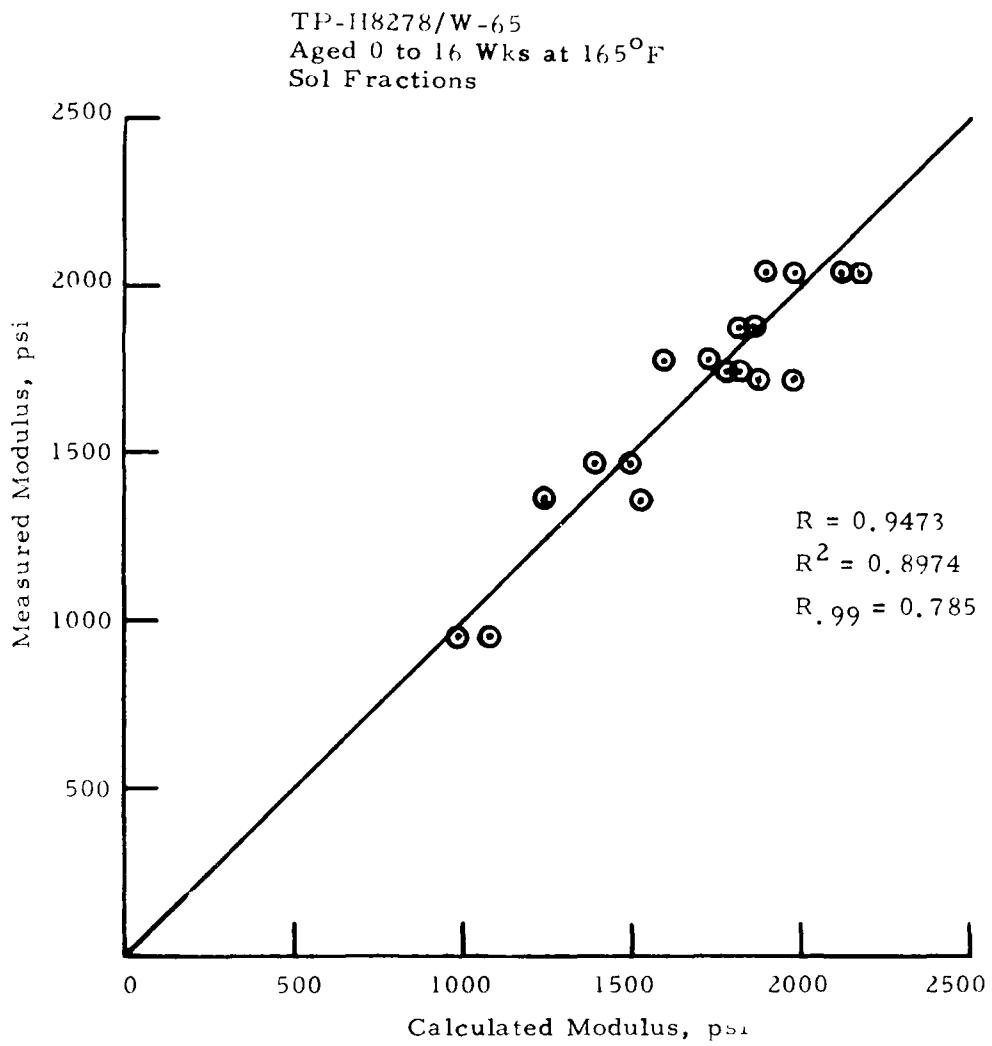
Figure 51. Multiple Correlation for Modulus

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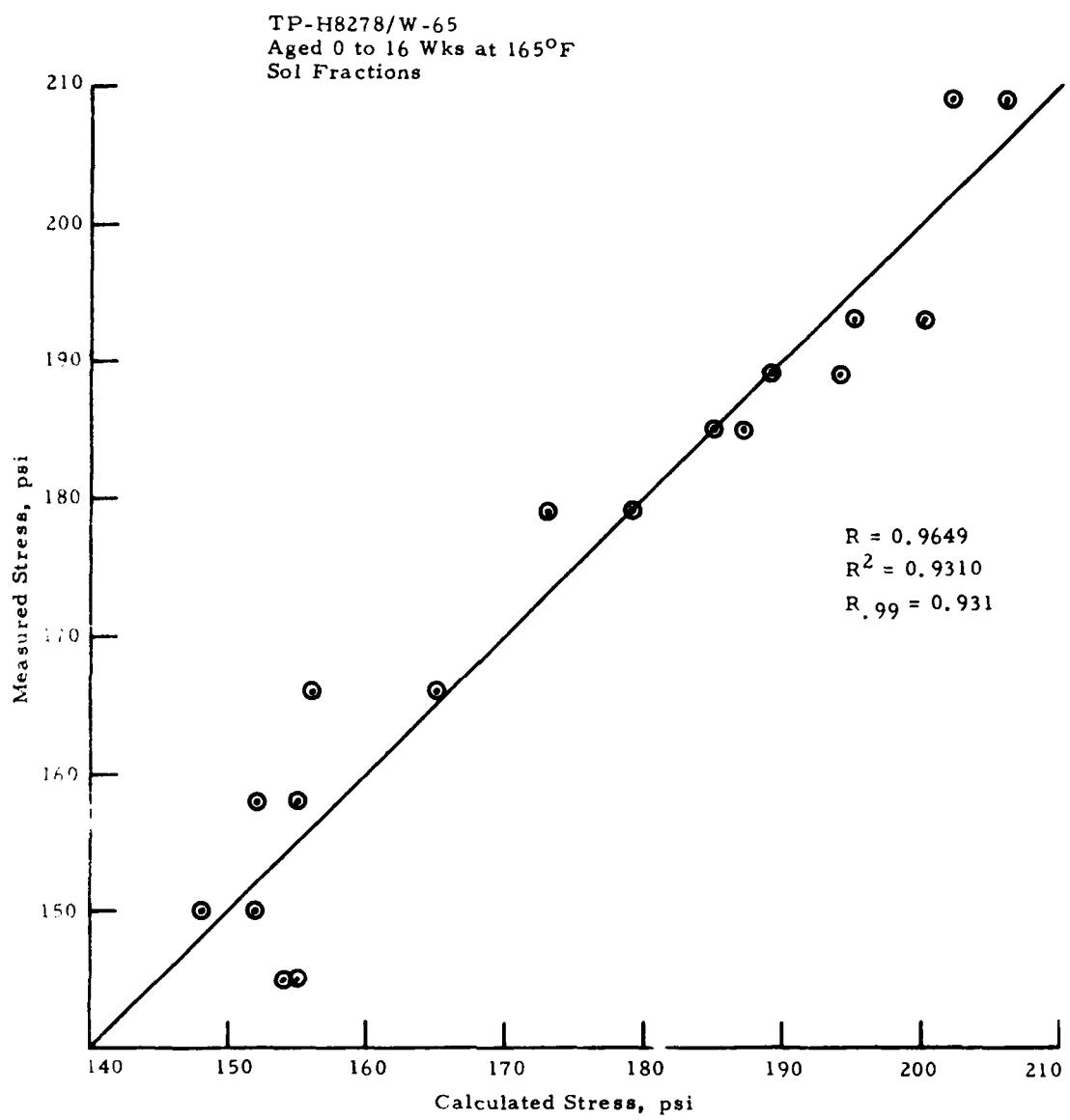
Figure 52. Multiple Correlation for Stress

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TP-H8278/W-65
Aged 0 to 16 Wk at 165°F
Sol Fractions

R = 0.8495
R^2 = 0.7217
$R_{.99}$ = 0.677
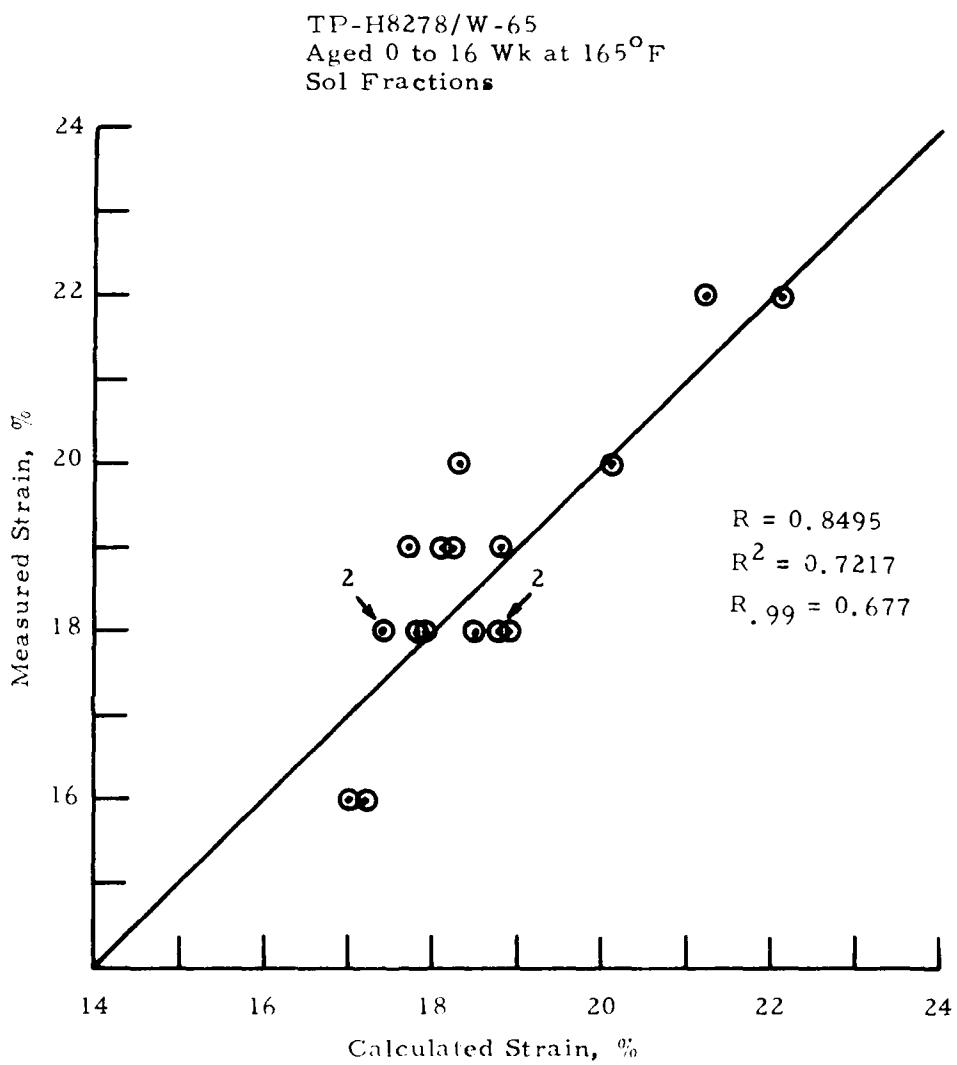
Figure 53. Multiple Correlation for Strain

TABLE 20

UNSATURATION IN LOW COST BINDER PROPELLANT

Chemical Aging - Unsaturation
W-65 (TP-H8278)

Time	Temp.	% Trans	% Vinyl	% Cis	Total
"0"	Amb	54.8	19.9	14.5	89.2
1.4 Wks	100°F	54.6	19.9	14.7	89.1
1.4 Wks	165°F	53.7	20.3	15.1	89.0
2 Wks	100°F	58.8	20.7	16.2	95.7
2 Wks	165°F	57.2	20.5	16.1	93.8
3 Wks	165°F	53.9	20.1	15.4	89.4
4 Wks	100°F	53.8	20.1	15.3	89.1
4 Wks	165°F	53.6	19.9	15.5	89.0
6 Wks	165°F	52.8	19.8	15.1	87.7
8 Wks	100°F	54.6	20.2	14.6	88.8
8 Wks	165°F	53.5	19.9	15.0	88.4
10 Wks	165°F	52.3	19.6	14.7	86.6
16 Wks	100°F	52.0	19.3	14.1	85.7
16 Wks	165°F	50.8	19.0	14.6	84.3

TD-H8278/W-65
Aged 0 to 16 Wk at 165°F
Sol Fractions
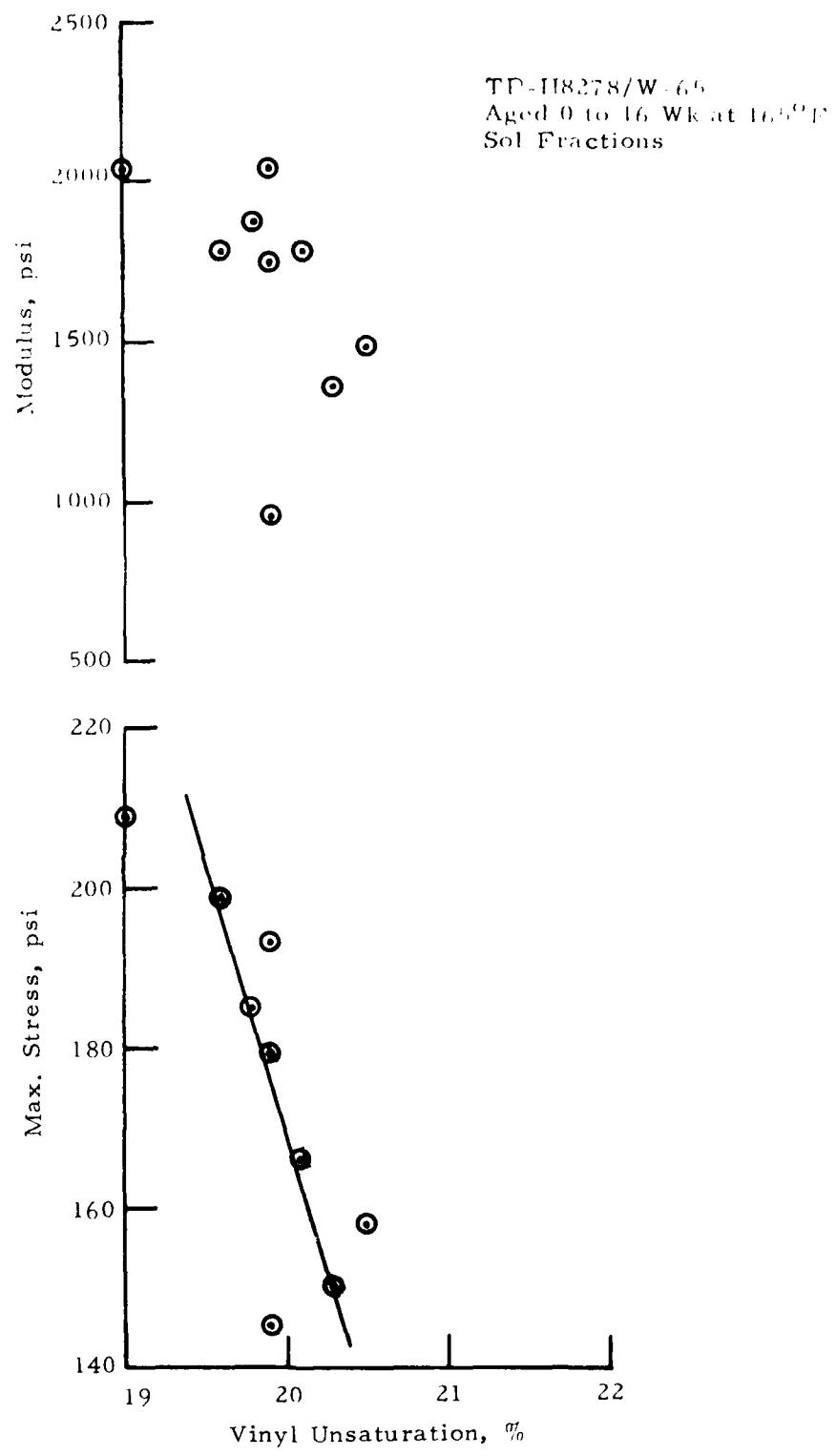
Figure 54. Relationship of Vinyl Unsaturation to Modulus and Stress

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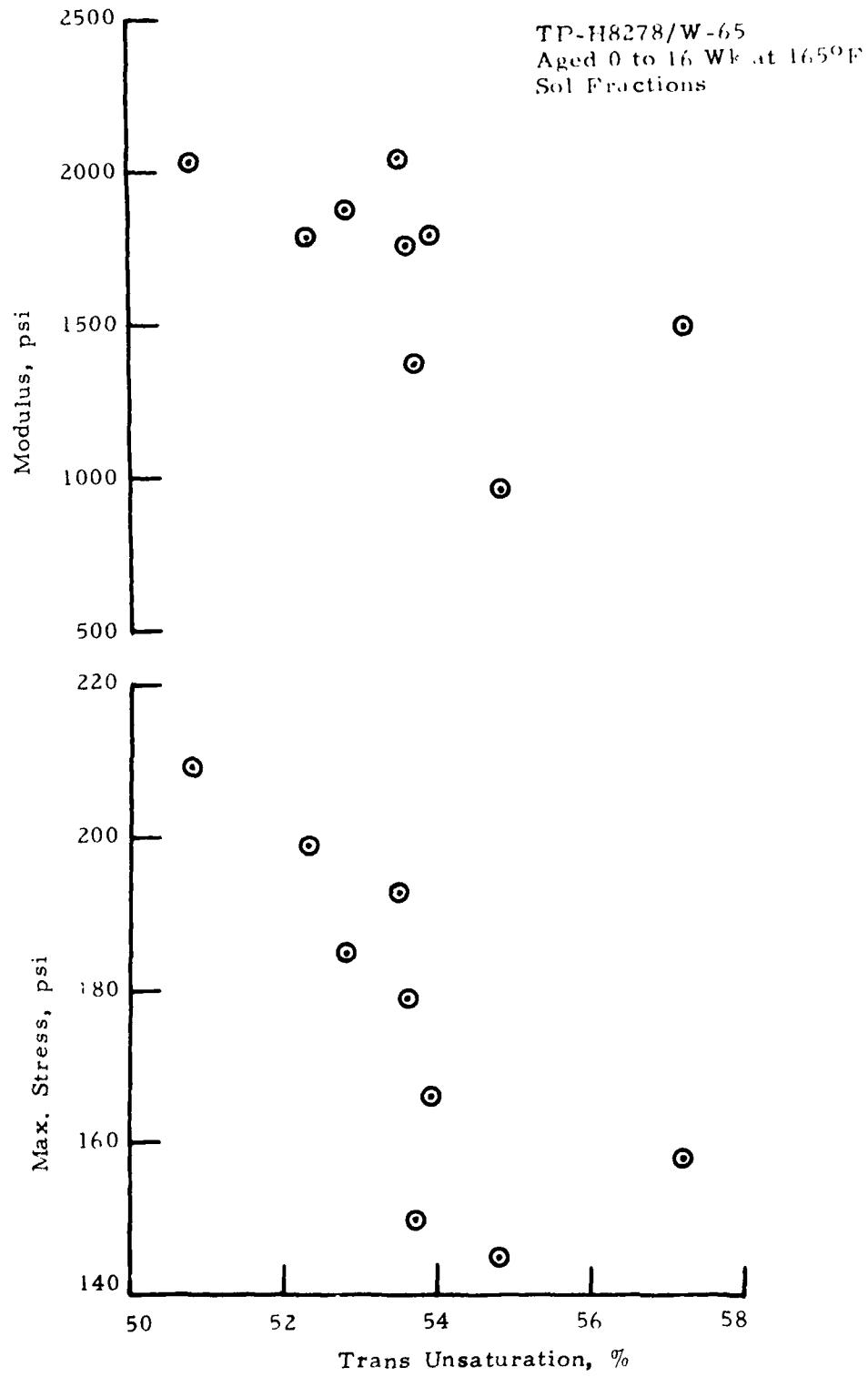
Figure 55. Relationship of Trans Unsaturation to Modulus and Stress

the quantity of unsaturation. The only strong correlation that is readily apparent in these data is the relationship between vinyl unsaturation and propellant maximum stress. Correlation coefficients were not calculated for these data.

AP-Leached Gel Fraction

Samples of TP-H8278 propellant from Mix W-65 were leached with water (to remove AP) using the standard technique, and these samples were then submitted to a gel/sol separation in which the propellant was leached with methylene chloride in a Sohxlet extractor to remove the sol fraction. Propellant that remained after this treatment was the gel fraction. Infrared spectra of these samples were measured.

Figure 56 is a typical spectrum of AP-leached TP-H8278 propellant gel fraction. This spectrum shows that there is a small amount of AP remaining in the gel fraction... small peak occurring at 3300 cm^{-1} and another occurring at about 1070 cm^{-1}. All of the plasticizer has been removed because the plasticizer peak located at approximately 1740 wave numbers is totally missing. The small peak occurring at 1715 to 1720 wave numbers is a part of the binder cross link structure.

After all spectra had been made and reduced by computer, peak heights and mechanical properties corresponding to each age time were the variables used in the statistical analysis program. Simple correlations from this statistical treatment are displayed in Table 21. There were only two peaks which bore a statistically significant correlation to a mechanical property (stress). The peak at 1643 is representative of unsaturation in general and the peak at 918 is representative of the vinyl unsaturation remaining in the binder gel fraction. For 8 observations a correlation coefficient of 0.71 is required for 95% confidence and a correlation coefficient of 0.83 is required for a 99% confidence level. The peak at 1643 fits into the former category while the peak at 918 cm^{-1} fits into the latter category.

A single multiple correlation was computed; that correlation concerns the change in height of the peak at 918 cm^{-1} and its relationship to stress. These and other pertinent data are displayed in Table 22. Correlation coefficient for this equation was 0.8556 and for 8 observations and 6 degrees of freedom a minimum correlation coefficient of 0.83 is required at the 99% level; therefore, the multiple correlation is significant at the 99% confidence level.

A plot of stress calculated with this equation against measured stress is shown on Figure 57. Although this is not one of the stronger correlations found in the course of this program, it does show that the AP-leached gel fraction of the propellant binder can be related to the mechanical properties of aged propellant.

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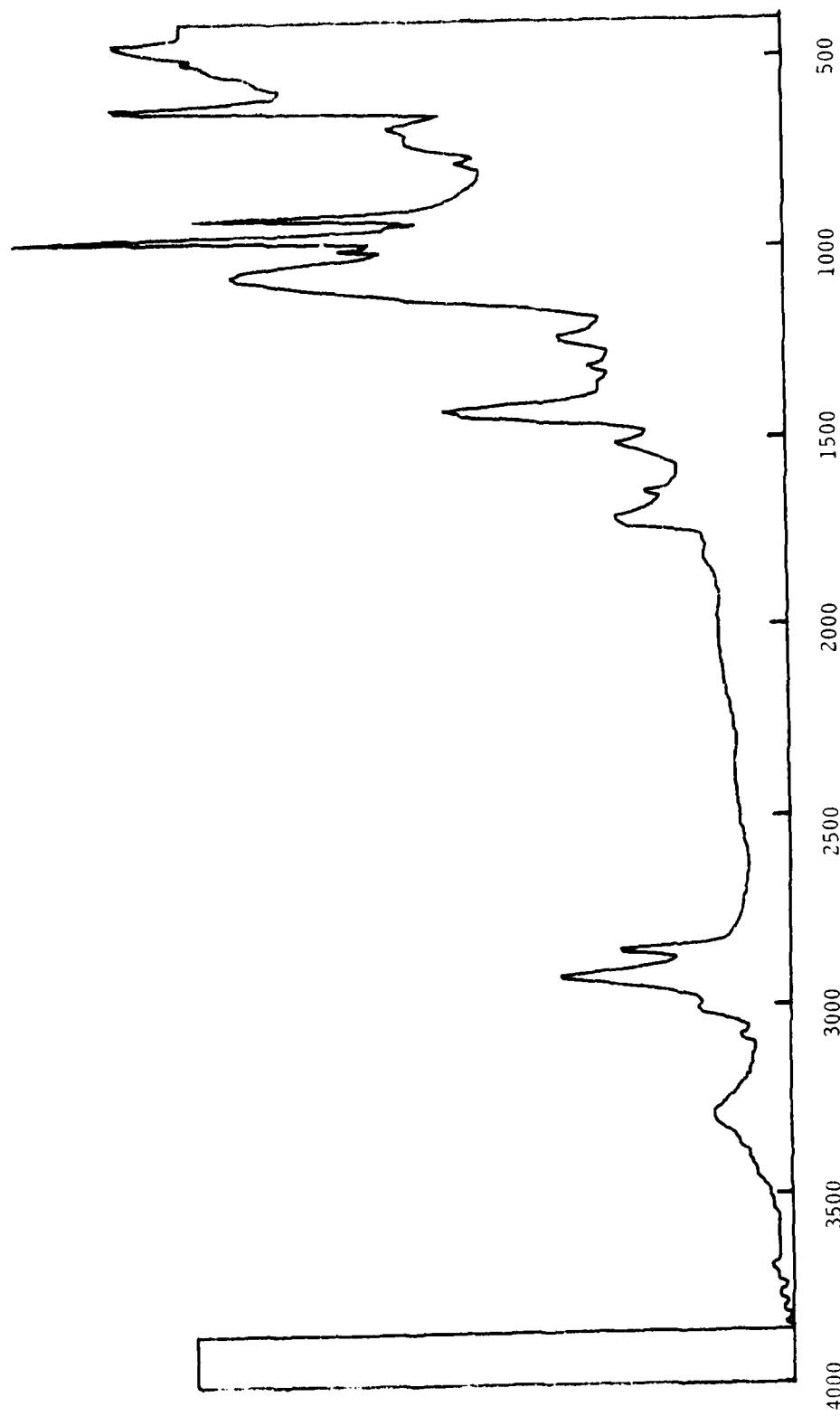
Figure 56. Typical IR Spectrum of TP-H8278/W-65 Gel Fraction of AP-leached Propellant (Propellant Aged Zero Time).

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TABLE 21

SIMPLE CORRELATIONS OF PEAK HEIGHT CHANGES

AND MECHANICAL PROPERTY CHANGES

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, AP-leached Gel Fraction)

Peak, cm^{-1}	Correlation Coefficient for Mechanical Properties		
	Modulus	Stress	Strain
1643		-0.8080	
918		-0.8556	

For 8 observations (no. of age time tests):

$R_{.95} = 0.71$

$R_{.99} = 0.83$

TABLE 22

MULTIPLE CORRELATION FOR PEAK HEIGHT

CHANGES AND STRESS

(TP-H8278/W-65, Aged 0 to 16 Wk at 165°F, AP-leached Gel Fraction)

STRESS = 395.1 - 6.120(X_9)

Where: X_9 = Height of Peak at 918 cm^{-1}

R = 0.8556

R^2 = 0.7321

Standard Error of Estimate Going In = 20.67 psi

Standard Error of Estimate w/Equation = 11.56 psi

For 8 observations and 6 degrees of freedom: $R_{.99} = 0.83$

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TP-H8278/W-65 Aged 0 to 16 Weeks at 165°F
AP-leached Gel Fraction

R = 0.8556

R^2 = 0.7321

$R_{.99}$ = 0.83

Stress = 395.1 - 6.120 (peak ht. at 918 cm^{-1})
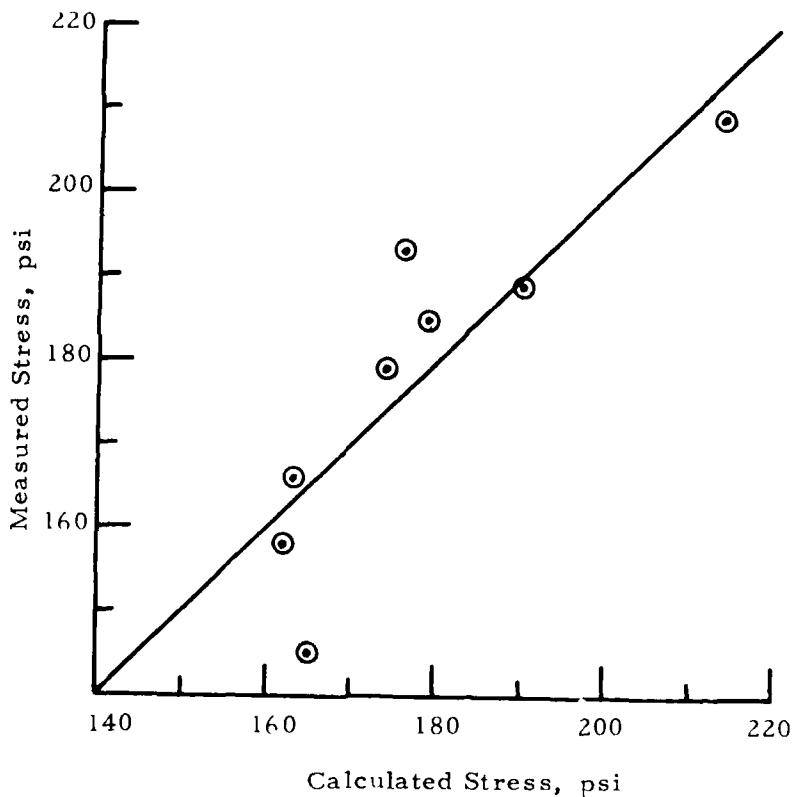
Figure 57. Multiple Correlation for Stress

IR Spectrum of HMX

Some additional studies have been made to determine the effect of how IR data are acquired on the quality of the resulting spectrum. The spectra of HMX at several particle sizes were made using the Barnes ATR apparatus in which different amounts of compression were used to establish contact between the HMX and the IRE (Internal Reflection Element) of the ATR unit. Three particle sizes of HMX were employed ... 5μ, 50μ, and 150μ.

The first study involved only 5 μ HMX and evaluated the effect of the amount of compression used in holding this small particle material against the IRE. Torque values of 8 oz-in and 16 oz-in were used to establish the two different compression levels. Figure 58 shows spectra made at the two compression levels, both plotted on the same graph.

A review of the two spectra revealed the following:

(a) There were no band shape changes between the two spectra

(b) There were some band width changes between the two spectra. There was a slight broadening on the low wave number side of all but the smallest of the peaks.

(c) There were no changes in the location (wave number) of the top most point of each absorption peak.

(d) There were some relative peak height changes because of the change in the torque on the assembly bolts for the ATR unit.

The amount of this relative change in four representative peaks on the spectrum was calculated by dividing the height of the peak at an assembly torque of 16 oz-in by the height of the same peak at an assembly torque of 8 oz-in. Table 23 shows the results of these computations.

With reference to the data in Table 23 it is entirely understandable that, as the contact between the sample and the IRE surface is improved that the absorption of infrared energy increases; this fact is observed. However, the change in absorption of energy should be a constant, but the data in Table 23 reveals that it is not a constant; it varies from peak to peak. Why this variation should occur is not understood, but the fact that the variation is not a constant must be taken into account when making spectra of propellants containing HMX.

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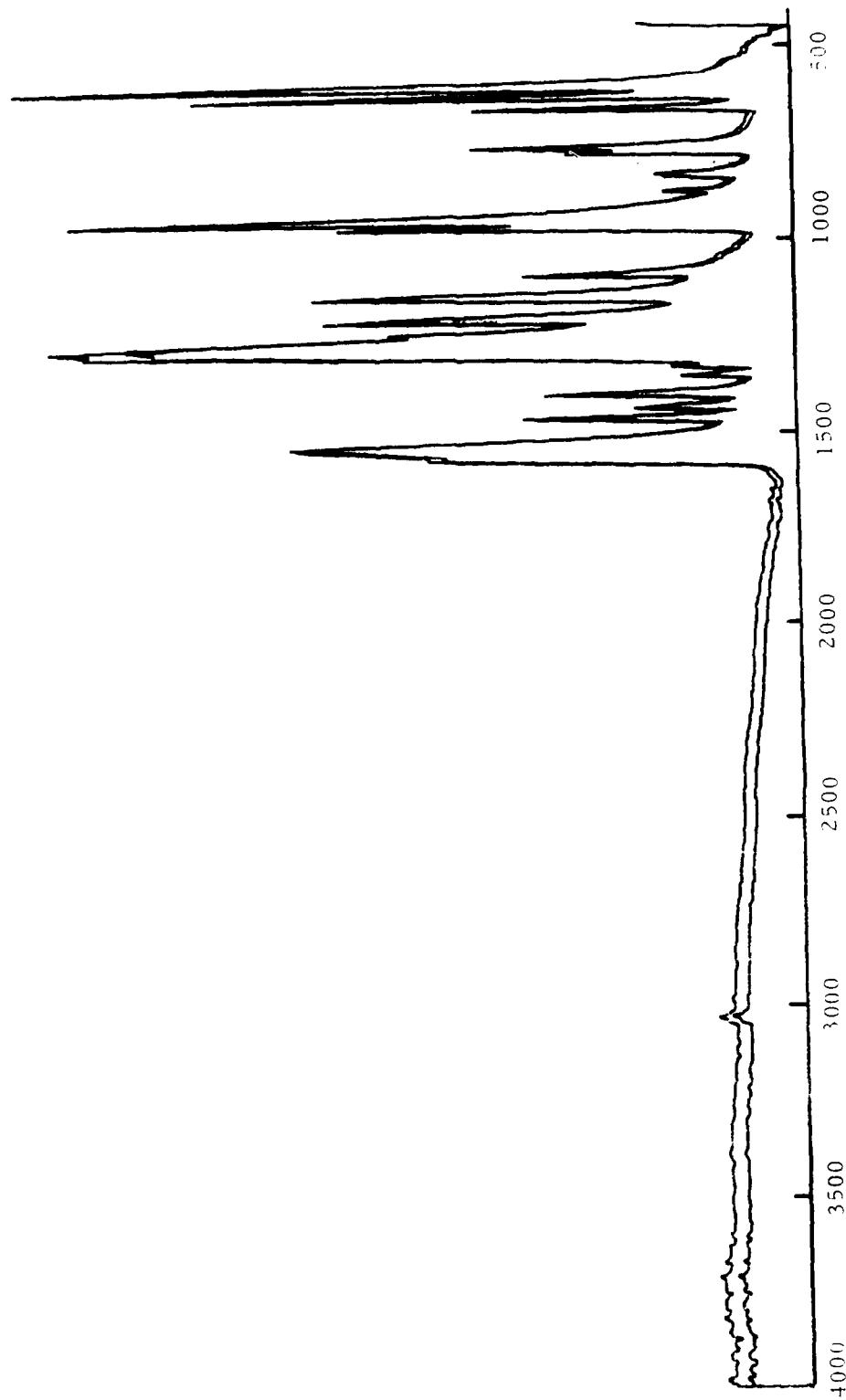
Figure 58. Infrared Spectra of 5μ HMX Made at Two ATR Unit Assembly Forces.
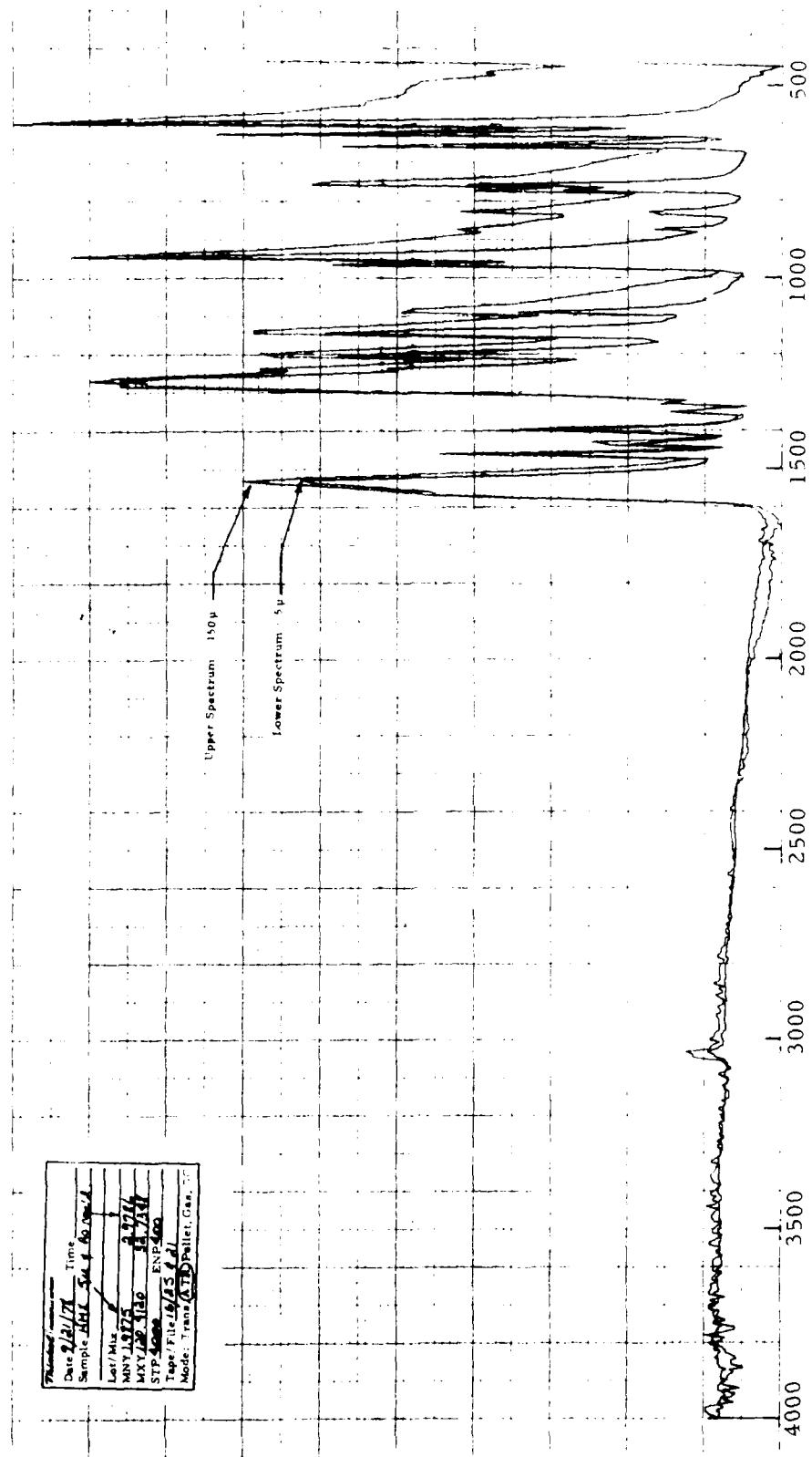
Figure 59. Infrared Spectra of 5μ, and 150μ HMX, Plotted With Scale Expansion.

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TABLE 23

EFFECT OF ASSEMBLY FORCE ON IR

SPECTRUM OF 5μ HMX

$$\Delta^* \text{ at } 1530 \text{ cm}^{-1} = \frac{128.7}{112.2} = 1.147$$

$$\Delta \text{ at } 1265 \text{ cm}^{-1} = \frac{155.0}{147.8} = 1.049$$

$$\Delta \text{ at } 1140 \text{ cm}^{-1} = \frac{103.0}{90.9} = 1.133$$

$$\Delta \text{ at } 765 \text{ cm}^{-1} = \frac{82.8}{69.4} = 1.193$$

$* \ \Delta = \dfrac{\text{height, mm, of peak in spectrum at 16 oz-in force}}{\text{height, mm, of peak in spectrum at 8 oz-in force}}$

A second study was made of the difference between spectra of 150 μ and 5 μ HMX, these two spectra are shown on Figure 59. Here we found band shape changes, band width changes, and changes in the location of absorption peaks. Shape changes occurred in the 1100 to 1000 cm^{-1} region, 940 to 800 cm^{-1} region, 750 to 660 cm^{-1} region, and 600 to 450 cm^{-1} region. Notice again that, in almost all instances, the band width change occurred on the low wave number side of each of the peaks. There were also some absorption peak changes, and these occurred at 1440 to 1430 cm^{-1}, 1205 to 1195 cm^{-1}, 1090 to 1080 cm^{-1}, and 840 to 830 cm^{-1}. These differences between the two particle sizes of HMX are similar to the changes that we have observed in AP when particle size is changed; therefore, in trying to subtract the spectrum of HMX from the spectrum of an HMX propellant, the effect of the HMX particle size will have to be taken into account when selecting an HMX spectrum to accomplish the subtraction.

A third study concerning the infrared spectrum of various particle sizes of HMX was made. We examined more closely the effect of particle size on the height of each of several peaks in the spectrum of HMX. Particle sizes of 5, 50, and 150 μ were examined and all spectra were plotted on the same scale. These spectra are shown on Figure 60.
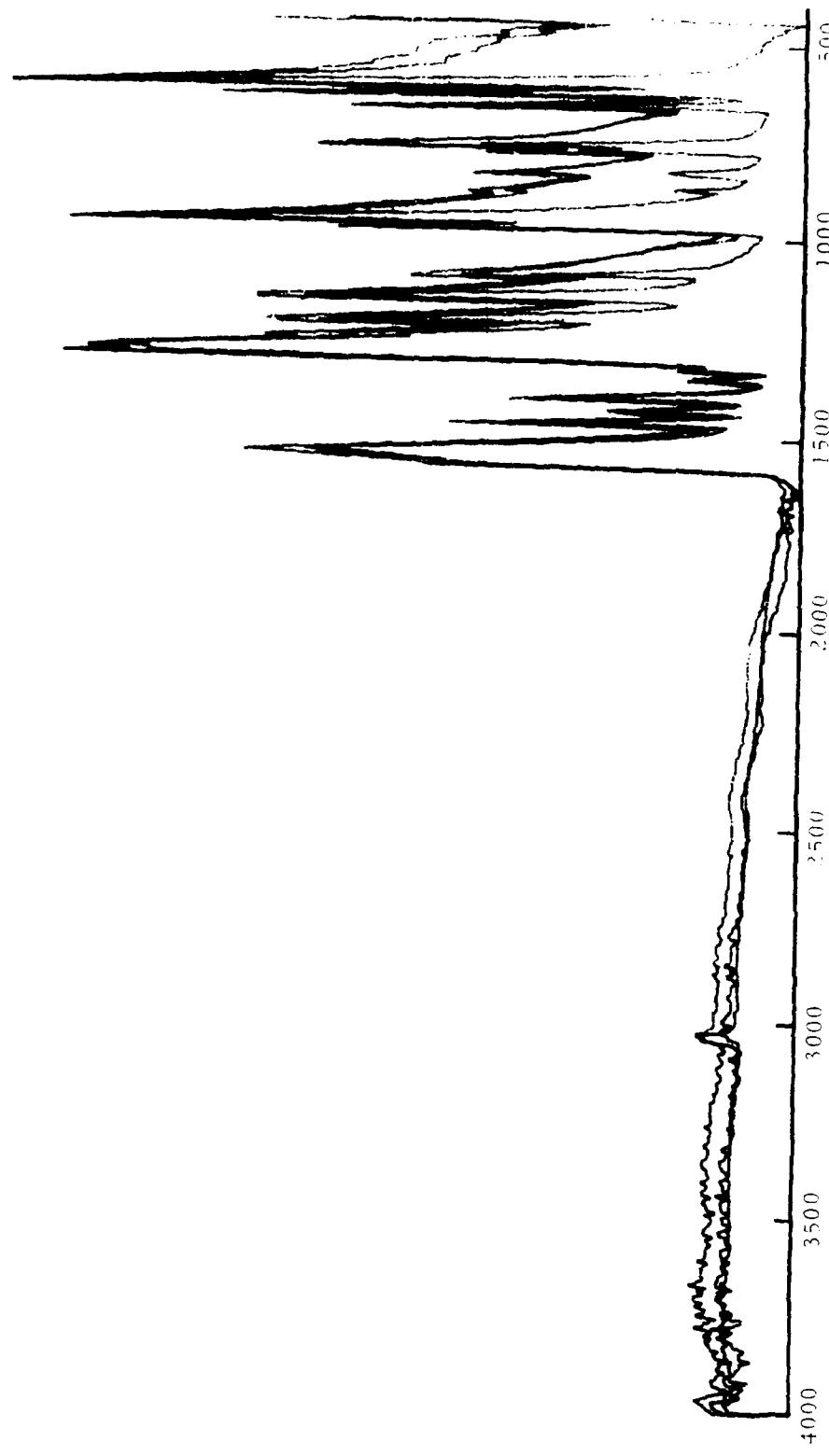
Figure 60. Infrared Spectra of 5μ, and 150μ HMX, plotted on the Same Scale.

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The heights of peaks at 1530, 1265, 1140, and 755 cm^{-1} were measured and the heights of the latter three peaks were ratioed to the height of the first peak for each of the three particle sizes. The ratio between a given pair of peaks should be the same regardless of the particle size of the HMX, but the data in Table 24 shows that this is not true. There is some variation in the ratio between any two given peaks as one moves from large to small particle HMX.

A second set of data comparisons was made to observe the change from particle size to particle size among the several peaks under consideration. These data are shown at the bottom of Table 24. Here the height of a peak in the 150 μ HMX was compared with the height of the same peak in the other two spectra. Here, if peak height change because of particle size change is uniform across the entire spectrum, then the ratio between, for example, 5 μ and 150 μ HMX for the four peaks the ratio should be a constant. ' ooking at the data at the bottom of Table 24 one sees that it is not a constant although the differences are small except for the ratio involving the peak at 1530 cm^{-1}. Overall, there is less change when one compares the 50 μ and the 150 μ HMX spectra. The ratios of the peak heights in the two spectra are fairly constant for the 50/150 μ HMX spectra except for the peak at 755 cm^{-1} and it is quite different from the other three.

TABLE 24

PEAK HEIGHT CHANGES BECAUSE OF PARTICLE SIZE

	$\dfrac{1265}{1530}$	$\dfrac{1140}{1530}$	$\dfrac{755}{1530}$
150 μ HMX	.9973	.6273	.5282
50 μ HMX	1.1519	.6822	.4883
5 μ HMX	1.1889	.7949	.6378

	$\dfrac{5\mu}{150\mu}$	$\dfrac{50\mu}{150\mu}$
1530 cm^{-1}	3.4638	1.1475
1265 cm^{-1}	4.1290	1.3253
1140 cm^{-1}	4.3889	1.2479
755 cm^{-1}	4.1827	1.0609

Subtraction of HMX from Propellant

A study of the feasibility of subtracting HMX from a propellant containing HMX was conducted. A very simple HMX propellant was made; it contained HMX and a binder composed of R-45M and IPDI. The formulation for this propellant is shown in Table 25. A gumstock containing only the polymer and its curing agent was made using the same cure ratio as employed in the propellant.

TABLE 25

HMX CONTAINING PROPELLANT
(DTS-9209, BP-2221)

R-45M	18.6
IPDI	1.4
HMX (55μ)	40.0
HMX (30μ)	24.0
HMX (5μ)	16.0

Infrared spectra of the propellant and the gumstock are displayed on Figures 61 and 62 respectively. The contributions of binder and HMX to each of the spectral peaks are shown on Figure 61. A review of the propellant spectrum (Figure 61) and several HMX spectra revealed that the band widths and peak locations were more like the spectrum of 50 μ HMX than either the 30 or 5 μ material that was also present in the propellant. A spectrum of the large-particle-size material is given on Figure 63, and the fact that the infrared spectrum of the 50 μ HMX closely approximates the band widths and peak locations of that material in the propellant spectrum shows that the propellant spectrum is dominated by the large particle HMX.

Subtraction of HMX from the spectrum of propellant was accomplished at three scaling ratios, SCB = 1, 1.5 and 2.0. These three subtractions along with the spectrum of the propellant itself are displayed on Figure 64. Virtually none of the subtractions furnished a spectrum that bore a precise relationship to the spectrum of the gumstock shown in Figure 62. There appeared to be too many chemical and/or spectral interactions between the binder and the HMX to make the subtraction of HMX from propellant useful for quantitative work.

Since in the FTIS project the subtraction of HMX from a propellant containing HMX represented only a small work effort and was included only with the intention of establishing the feasibility of this subtraction, we did not

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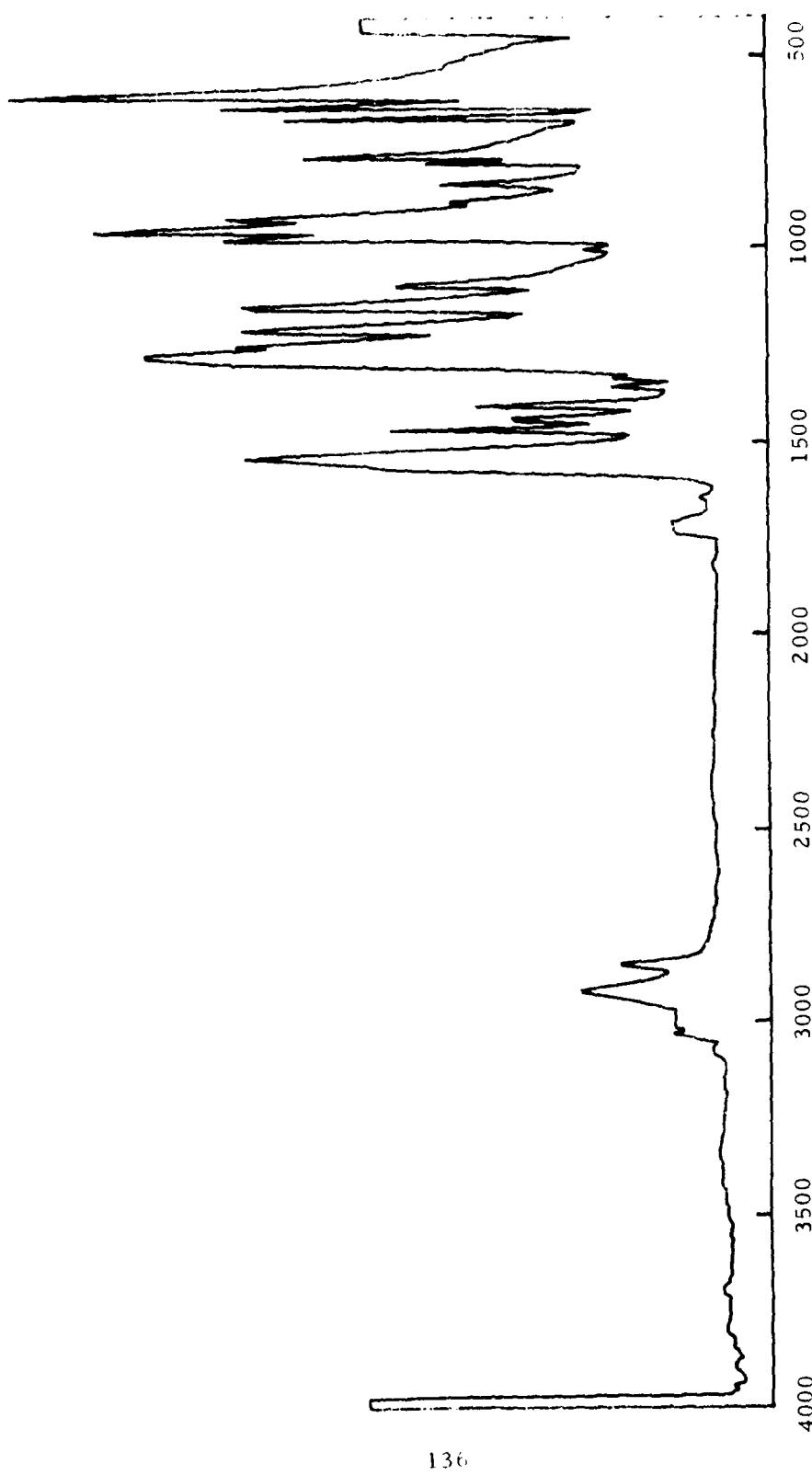
Figure 61. IR Spectrum of Propellant Containing HMX
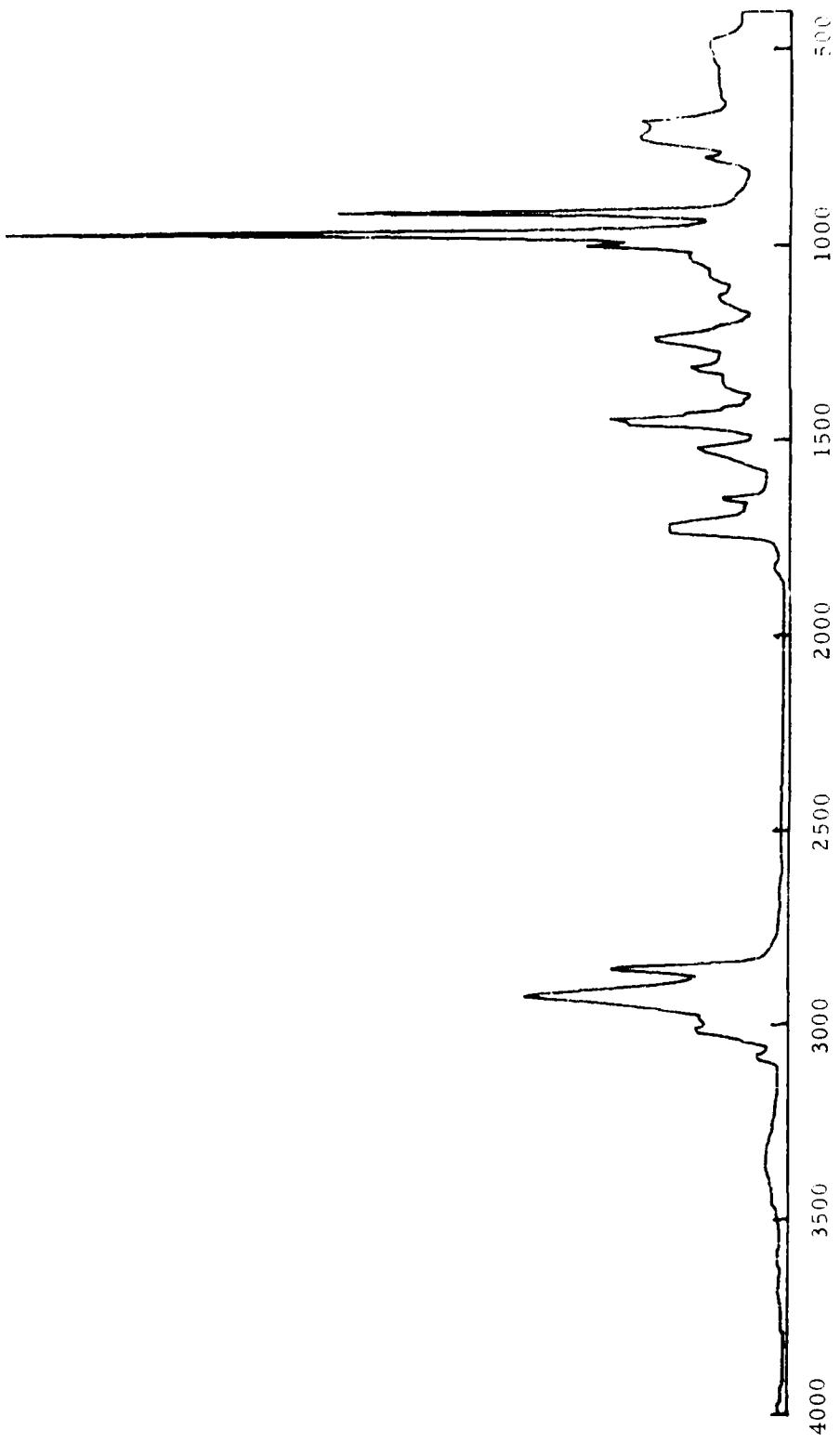
Figure 62. IR Spectrum for R-45M/IPDI Gumstock

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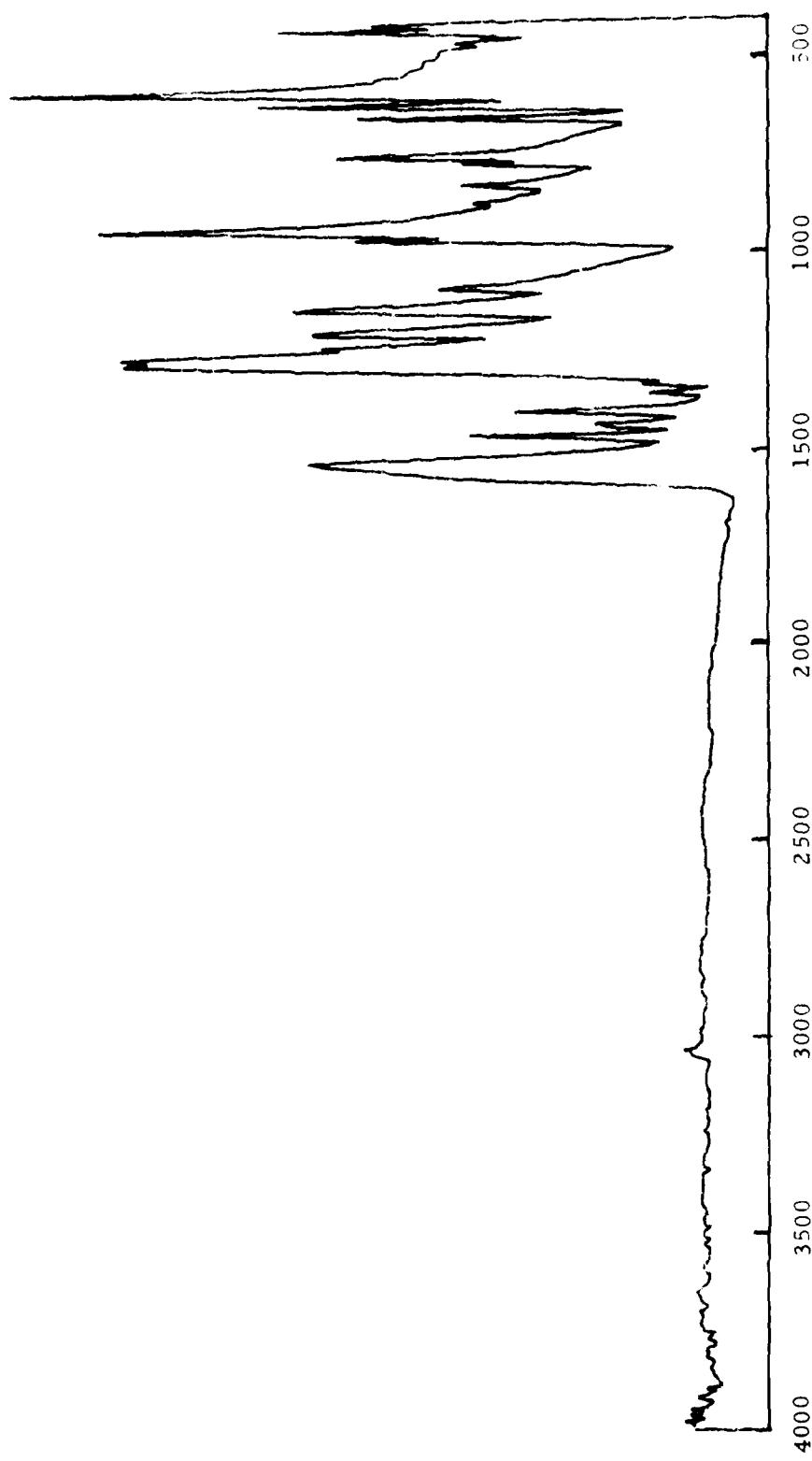
Figure 63. IR Spectrum of 50 μ HMX
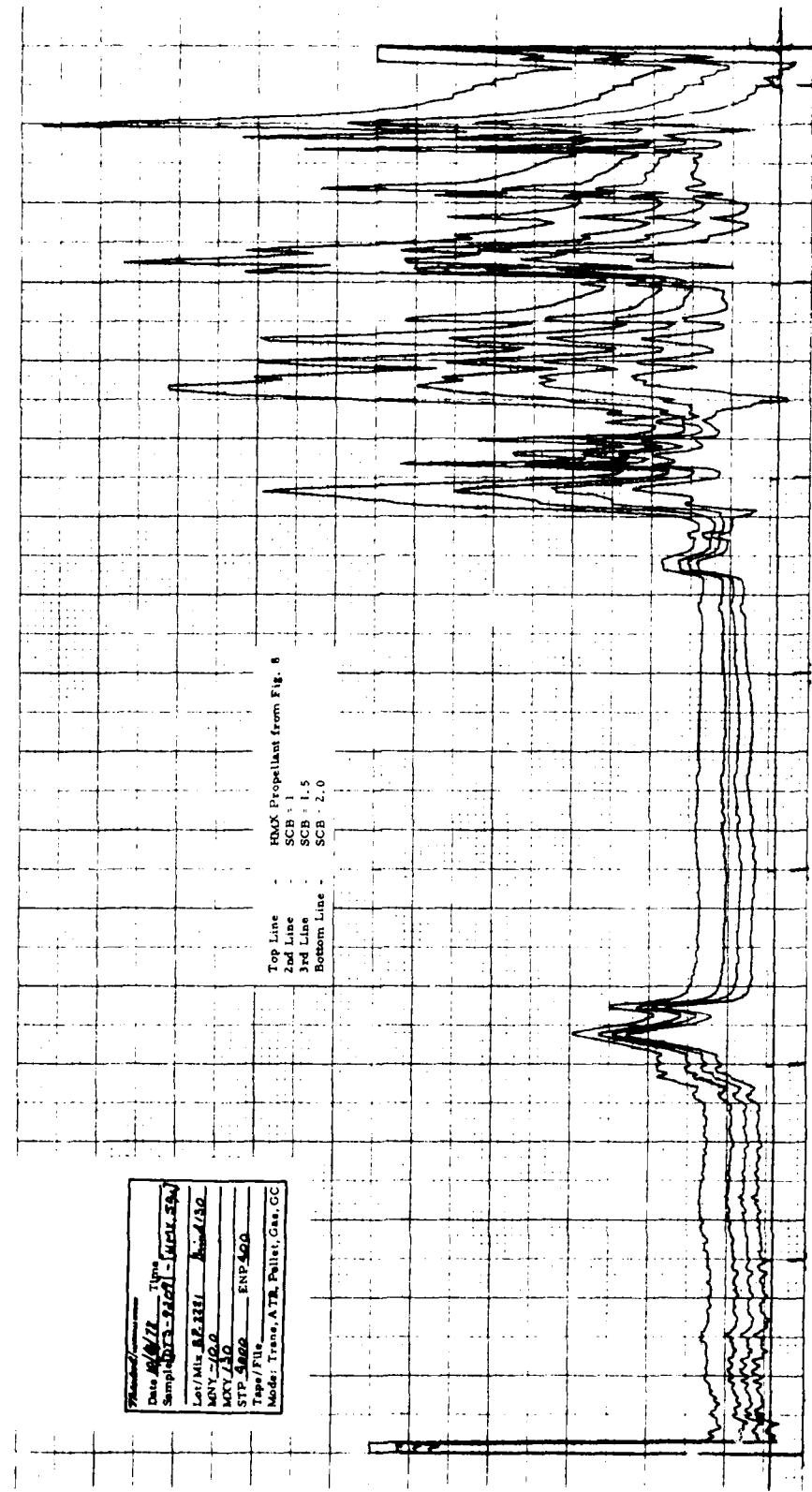
Figure 64. HMX Subtracted From HMX Propellant (Figure 61) at
Various Scaling Factors

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pursue this further. For the purposes of the FTIS project, we concluded that the subtraction of HMX from propellant will be an exceedingly difficult thing to accomplish, but probably not an impossible task.

IR Data Acquisition Standard Procedures

Following are the conclusions drawn from the Phase I, Task 2 effort to identify the proper procedure for acquiring IR data.

1) Microtome sample (0.01 - 0.02 inch thick).

2) Barnes ATR, 45° angle of incidence.

3) KRS-5 IRE, 45° entrance angle.

4) Assembly pressure set so that:

    a) For whole propellant MXY = 80 to 130

    b) For AP-leached propellant MXY = 50 to 100

5) Torque assembly bolts evenly and in small increments so that maximum "foot print" is achieved.

6) Position IRE same direction and in same location each time.

7) Use same IRE each time.

8) If a sample is "over-torqued", a fresh sample must be used.

9) Do not subtract plasticizer spectrum from spectrum of propellant.

10) Do not subtract AP spectrum from spectrum of propellant.

11) Subtraction of the spectrum of aluminum from spectrum of propellant is optional.

12) Leaching of AP from propellant is optional.

13) If (11) and (12) are done for one sample, they must be done for all samples in a data set.

Task 3 - Testing

Task 3 of this phase was for the purpose of evaluating the IR data acquisition method selected at the end of Task 2 of Phase I. That data acquisition method stipulated the use of the Barnes ATR unit with a KRS-5 IRE, the use of whole propellant, and no subtraction of plasticizer. Subtraction of the spectrum of aluminum from spectra of propellant was an option;

however, if aluminum was subtracted from one propellant it must be subtracted from all propellant spectra employed in a correlation data set. This follows the general rule that all spectra in a correlation data set must have been created using identical procedures and the data reduced using identical procedures.

Two propellants were evaluated using the selected data acquisition method ... TP-H8156 and TP-H8266. These two propellant had been aged 12 months as parts of other projects. TP-H8156 had been aged as a part of an Army project and TP-H8266 as a part of an IR&D program. During both of the projects, the IR spectra of the propellants had been acquired using a procedure which closely approximated the selected one up to the point in the FTIS project where an acquisition method was selected. From that point on, in these other projects, the IR data acquisition method was the one selected in the FTIS project. Where the old IR data had not been acquired by the selected method and were vastly different, new spectra were made using samples which had been frozen to prevent further aging.

Detailed discussions of the correlations found for these two formulations are presented in Appendix E for TP-H8156 and in Appendix F for TP-H8266.

General conclusions drawn from this work are as follows:

1) The IR data acquisition method is satisfactory.

2) Computer program E-490 for IR data reduction works quite well, and at near the maximum number of spectra that it is capable of handling, it performs the data reduction in less than five minutes.

3) The statistical data analysis program works well and successfully reduced all of the statistical data presented.

4) Subtle differences in the IR data reduction procedures do not completely destroy the simple correlations, but they do, however, introduce new correlations and do eliminate other correlations. These subtle differences do change multiple correlations.

5) Multiple correlations reveal something of the chemistry of aging and may be valuable for the prediction of age life.

6) The simple correlations reveal quite a bit about the chemistry of aging and will be useful in predicting age life.

7) The data variations that were found indicate a very strong need for a study of the reproducibility of the method by which the IR data are acquired.

PHASE II - SERVICE LIFE PREDICTION

Task 1 - Propellant Preparation

Several propellant formulations suitable for aging in the FTIS project were reviewed and two were selected. These two formulations, TP-H8278 and DTS-9589, were recommended to and approved by AFRPL for the project. The general ingredients of the two propellants are listed in Table 26.

Propellant TP-H8278 was developed on the Low Cost Binder project (Contract F04611-77-C-0028) and was to be subjected to an aging program beginning in October of 1978. This schedule allowed a full one year of aging to be completed during the technical life of the FTIS project. This formulation was of interest to the FTIS project because of its small number of ingredients and the opportunity to observe the chemical behavior of a new bonding agent, bis phenol A diglycidyl ether (BPA). The fewer the number of ingredients in the formulation, the fewer the number of aging reactions and, therefore, the better the chance of observing these reactions in the IR and correlating them with changes in the propellant's mechanical properties.

Propellant DTS-9589 was developed on another project (Contract F04611-78-C-0007) and was to have started into an aging program in November of 1978. Because of unexpected LCMM project delays on the other project, the aging of this second propellant did not start until April 1979.

Propellant for the FTIS project aging of TP-H8278 was made in Mix W-65 under Contract F04611-77-C-0028, while the propellant for the aging of DTS-9589 was prepared in Mix T-991 under this project.

TABLE 26

FORMULATION OF TP-H8278

Ingredient	Amount
R-45HT/MAO } IPDI	10.85
BPA	0.15
DOA	1.00
Al	18.00
AP	70.00

FORMULATION OF DTS-9589

Ingredient	Amount
R-45HT/MAO } IPDI	9.20
DQC	0.05
BPA	0.15
DOP	3.00
AP	85.50
ZrC	1.00
Fe_2O_3	0.60
Graphite Flakes	0.50

Task 2 - Aging and Testing

Propellant TP-H8278

Propellant TP-H8278 was aged, for the FTIS project according to the plan shown in Table 27. Partially filled 1/2-gallon cartons of the propellant were sealed with aluminum foil, placed in a metal can, flushed with dry nitrogen, then the can was sealed. At each test interval, a carton was removed for tensile testing. Infrared spectra of the propellant were made at each designated test interval using the remnants from cutting the JANNAF tensile specimens. An infrared spectrum was made and stored on magnetic tape as an absorbance spectrum. These spectra were later used in the correlation of IR peak height changes with propellant mechanical property changes and changes in time.

Mechanical properties of the aged propellant are given in Table 28. Although the aging characteristics of this propellant were not of primary concern to this project, it is appropriate to make some comments. Very little hardening appeared to occur in the bulk samples stored at 77°, 100°, and -65 F. Modulus, stress and strain values remained the same for about three to four weeks into the aging. At the two higher temperatures, 145° and 165°F, the propellant continued to harden beyond this three to four-week period for the remainder of the 52 weeks of aging. Details concerning the aging of this formulation may be obtained in report AFRPL-TR-79-38.

Propellant DTS-9589

Propellant DTS-9589 was aged according to the plan shown in Table 29. Filled 1/2-gallon cartons of propellant were stored in the manner described for TP-H8278. At each test interval a carton was taken from storage, three 0.5-inch thick slabs were cut from the carton and the carton sealed and returned to its aging conditions. The first of the three slabs cut was discarded and three JANNAF specimens cut from each of the remaining two slabs. Tensile tests were performed on these six specimens. An IR spectrum was made of the propellant at each age time/temperature and was stored on magnetic tape, as an absorbance spectrum, for use in correlating IR spectral changes with propellant mechanical property changes.

Mechanical properties at each of the test intervals for the 20-week storage period are displayed in Table 30. Storage of the propellant at 145°F over the 20 weeks resulted in an overall increase in modulus, decrease in strain, and increase in maximum stress. Propellant stored at 165°F showed the same general characteristics with there being relatively little difference in the aging behavior of the propellant at the two temperatures.

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TABLE 27

AGING PLAN FOR TP-H8278 PROPELLANT

(Mix W-65)

Study	Sample Type	Temp., °F Storage	Test	0	1.4	2	3	4	6	8	10	16	26	36	52
Bulk Aging	Bulk	77	77	6	3	3	3	3		3		3	3	3	3
	Sealed	100	77		3	3	3	3	3	3		3	3	3	3
		145	77		3	3	3	3	3	3	3	3	3	3	3
		165	77		3	3	3	3	3	3	3	3	3	3	3
		-65	77					3				3	3	3	3

Test Time in Weeks and Number of Specimens to be Tested

TABLE 28

AGING CHARACTERISTICS OF TP-H8278/W-65

Mechanical Properties At Aging Temperature [a]

Aging Time, wks	77°F Mod., psi	77°F Strain at MS, %	77°F Max. Stress, psi	100°F Mod., psi	100°F Strain at MS, %	100°F Max. Stress, psi	145°F Mod., psi	145°F Strain at MS, %	145°F Max. Stress, psi	165°F Mod., psi	165°F Strain at MS, %	165°F Max. Stress, psi	-65°F Mod., psi	-65°F Strain at MS, %	-65°F Max. Stress, psi
0	946	22	145												
1.4	1365	17	138	1283	19	13.	1345	16	135	1360	20	150			
2				1274	18	137	1259	19	149	1480	19	158			
3	1404	15	134	1161	18	137	1499	16	149	1784	16	166			
4	1361	17	143	1389	16	137	1527	16	157	1747	18	179	1387	17	142
6							1674	16	164	1870	18	185			
8	1354	16	135	1335	10	139	1683	18	173	2040	18	193			
10							1681	20	176	1781	19	189			
16	1345	18	142	1447	18	145	1812	19	191	2036	18	209	1325	18	145
26	1288	16.9	138	1398	15	142	1945	15.5	190	2275	14	200	1252	16.7	139
36	1493	12.9	126	1605	11.9	139	2175	14.2	191	2363	13.2	202	1345	16.4	137
52	1394	15.5	138	1611	13.5	150	2334	14.6	198	2662	11.8	203	1469	16.8	140

[a] All tensile tests conducted at 77°F.

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TABLE 29

AGING PLAN FOR DTS-9589/MIX T-991

Aging Time, Weeks	Aging Temperature	
	145°F	165°F
0	X	X
1	X	X
2	X	X
4	X	X
8	X	X
12	X	X
16	X	X
20	X	X

NOTES:

1) Measure uniaxial tensile properties at 77°F, 2.0 in/min crosshead speed.

2) Test 6 JANNAF specimens at each time/temperature interval.

3) At zero time test 12 JANNAF specimens, 6 from each of two cartons. One carton will then be aged at 145°F and one at 165°F.

4) Place 3 cartons in aging at each temperature, this number includes the partial carton remaining from the zero time test (note 3).

5) At each time/temperature test period, cut 3 slabs from a carton, discard the first slab and test the remaining two slabs. Seal, with aluminum foil and tape, the surface of the propellant remaining in the carton and return it to the aging oven for use at the next test period.

6) Retain remnants from cutting the JANNAF specimens for FTIS.

TABLE 30

AGING CHARACTERISTICS OF DTS-9589 PROPELLANT

(Mix T-991)

Age Time, Wk.	Stored at 145°F					Stored at 165°F				
	Modulus, Psi	Ult. Strain, %	Strain at MS, %	Max. Stress, Psi	Strain Energy Density	Modulus, Psi	Ult. Strain, %	Strain at MS, %	Max stress, Psi	Strain Energy Density
0*	398.7	38.45	33.37	100.84	20.55					
0	382.1	37.41	33.22	99.63	2C.10	415.3	39.50	33.51	102.05	21.00
1	564.5	31.65	28.41	121.05	21.40	692.9	32.90	29.75	137.61	26.64
2	668.0	33.81	29.54	133.48	25.82	889.5	29.24	27.01	151.90	28.12
4	733.6	32.56	30.09	163.04	30.88	973.5	31.59	30.00	198.81	38.00
8	842.7	30.47	29.04	182.10	32.83	1058.3	27.49	26.38	213.15	33.97
12	1055.2	26.10	24.92	189.73	29.19	1233.7	24.65	23.56	211.90	30.50
16	991.3	31.05	29.20	195.96	36.89	1227.7	24.77	23.93	210.44	30.95
20	1173.0	23.93	23.18	204.88	28.30	1169.3	25.04	24.21	217.50	31.51

Notes: 1) All tensile tests at 77°F.

2) Six specimens tested at each time/temperature interval.

3) Twelve specimens tested at zero time: six from a carton later stored at 145°F and six from a carton later stored at 165°F.

* Average of 12 specimens.

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Task 3 - Prediction

Prediction Based on Property Changes with Time

One of the prediction procedures planned for the program was a curve extrapolation and that method was used to make the first predictions of aging characteristics for TP-H8278. Table 31 shows the properties that would be predicted for the propellant and the properties that w_re actually measured at 26 weeks of aging. Extrapolation was made on a linear-linear plot of the propellant properties using the last two aging values for the extrapolation. A review of the data shown in Table 31 reveals that there is only one prediction (strain at maximum stress for aging at $100^\circ F$) that deviates greatly from the actual value found at 26 weeks of aging. Prediction of 30% strain was based on the behavior of the propellant during the previous two aging periods, those being at 8 weeks and 16 weeks. At 8 weeks, strain at maximum stress was 10% while at 16 weeks, the strain was measured at 18%. This gave a very steep upward slope to the prediction line. Strain at 8 weeks was considerably lower than strain values for all other age temperatures at that time and it is believed that is "bad" data, and this "bad" data certainly led to a very poor prediction.

A summary of the percent error in predictions made by this method is given in Table 32. Modulus seemed to be predictable to within 3.7% with all predictions being on the low side. Strain at maximum stress predictions had an average error of 31.2%, but primarily because of the questionable data at $100^\circ F$ storage. Leaving out the $100^\circ F$ storage data point reduces the average error to 14.0%; again, all predictions were on the low side. Maximum stress predictions had an average error of 11.6% over the measured data with all predictions being low.

A prediction was made for the properties of this propellant after 36 weeks of aging, with the prediction being made before 36 weeks was reached. Again, the predictions were based upon a straight line extrapolation made on a linear-linear plot of the previous two aging values. For this 36-weeks prediction, the previous aging values were 16 weeks and 26 weeks. A comparison of the predicted mechanical properties and the measured mechanical properties after testing at 36 weeks is shown in Table 33. Table 34 displays the error associated with each of the predictions that was made. The average error associated with the prediction of maximum stress was 3.18%. For strain, the error was 13.38% and for modulus, the error was 11.04%. Thus, the prediction at maximum stress was by far the most accurate with the method that was employed. This observation is contradictory to the observation on the 26-week prediction.

There are several things wrong with predicting by this method, not the least of which is that the method does not use infrared data. This fact

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TABLE 31

PREDICTED AND ACTUAL PROPERTIES FOR TP-H8278/W-65

AT 26 WEEKS OF AGING

	Predicted/Actual Values at Aging Temperature				
	-65°F	77°F	100°F	145°F	165°F
Modulus, psi	1270/1252	1325/1288	1550/1398	2000/1945	2285/2275
Strain at MS, %	19/16.7	20/16.9	30*/15	17/15.5	16/14
Max. Stress, psi	147/139	152/138	152/142	216/190	243/200

NOTES: 1. Prediction based upon extrapolation of a linear-linear
plot of the previous two "aging" values, as follows:

for 165°F, 10 weeks and 16 weeks.
for 145°F, 10 weeks and 16 weeks.
for 100°F,   8 weeks and 16 weeks.
for 77°F,   8 weeks and 16 weeks.
for -65°F,   4 weeks and 16 weeks.

At 8 weeks aging, strain at maximum stress was much lower
than values for propellant aged at all other temperatures.
It is believed that this value was "bad" data and certainly led
to a very poor prediction.

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TABLE 32

PREDICTION ERROR ASSOCIATED WITH TP-H8278

PROPERTIES AT 26 WEEKS OF AGING

	Prediction Error, % at Aging Temperature				
	$-65^\circ F$	$77^\circ F$	$100^\circ F$	$145^\circ F$	$165^\circ F$
Modulus	-1. 4	-2. 9	-10. 9	-2. 8	-0. 4
Strain at M. S.	-13. 8	-18. 3	-100	-9. 7	-14. 3
Maximum Stress	-5. 6	-10. 1	-7. 0	-13. 7	-21. 5

NOTES:

1) $\% \text{ error} = \dfrac{\text{Actual - Predicted}}{\text{Actual}} \times 100$

2) "-" indicates a low prediction.

3) "+" indicates a high prediction.

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TABLE 33

PREDICTED AND ACTUAL MECHANICAL PROPERTIES OF TP-H8278
(W-65) AT 36 WEEKS OF AGING

	Predicted/Actual Values at Aging Temperature				
	-65°F	77°F	100°F	145°F	165°F
Modulus, psi	1175/1345	1250/1493	1350/1605	2075/2175	2500/2363
Strain at MS, %	16/16.4	16/12.9	12/11.9	12/14.2	10/13.2
Max. Stress, psi	135/137	135/126	140/139	188/191	192/202

TABLE 34

PREDICTION ERROR

	Prediction Error, % at Aging Temperature				
	-65°F	77°F	100°F	145°F	165°F
Modulus	-12.6	-16.3	-15.9	-4.6	+5.8
Strain at M.S.	-2.4	+24.0	+0.8	-15.5	-24.2
Max. Stress	-1.5	+7.1	+0.7	-1.6	-5.0

1) $\%\ \text{Error} = \dfrac{\text{Actual} - \text{Predicted}}{\text{Actual}} \times 100$

2) - indicates low prediction

3) + indicates high prediction

defeats one of the major objectives of the project ... predict propellant mechanical properties on the basis of infrared spectral data. Another problem is that propellant mechanical properties do not respond to or correlate with time in a linear relationship, but rather in a curvilinear fashion that is best described mathematically by the logarithm of time and the logarithm of the mechanical property value.

A logarithmic relationship for the properties of TP-H8278 with time was computed and then used for a comparison with a similar relationship among propellant property/spectral data/time. This comparison is discussed in the next section.

Correlation and Prediction of Property Changes Based on IR Spectral Data

It has already been established that is is possible to identify the properties of propellant in a rocket motor from the infrared spectrum of a sample of that propellant. However, it was important to make a prediction of the propellant mechanical properties solely on the basis of infrared spectral information to meet the objectives of this project.

A mathematical approach to accomplishing this prediction was derived using a single peak in the infrared spectrum and using a multitude of peaks in the infrared spectrum. Taking the case of the single peak height first, we showed mathematically how prediction can be accomplished. Then we applied the same principles to the prediction of propellant properties from a multiple correlation in which several peaks respond to the changes in mechanical properties.

Prediction of changes in propellant mechancial properties is most easily accomplished if there is a single peak or several single peaks that undergo magnitude changes with the mechanical property changes. In order to make the prediction, there must also be a correlation of the changes in that same peak with changes in time. Take, for example, the correlation of changes in a peak height with changes in stress and time. It involves two equations with the coefficients of each equation determined in independent calculations from the same set of infrared spectra. The relationship of peak height change to changes in time can be expressed by equation (1) while the correlation between the changes in that same peak height with changes in stress are expressed in equation (2).

$$f(\text{peak height}) = b_0' + b_1' f(\text{time}) \qquad (1)$$

$$f(\text{stress}) = b_0'' + b_1'' f(\text{peak height}) \qquad (2)$$

Substituting equation (1) into equation (2) gives the following expression.

$$f(stress) = b_0'' + b_1'' \quad b_0' + b_1'' \, f(time) \tag{3}$$

Equation (3) can be reduced to:

$$f(stress) = C + Df(time) \tag{4}$$

In equation (4) $C = b_0'' + b_1'' \, b_0'$ and $D = b_1'' \, b_1'$. Note that equation (4) has the form of the equation representing the correlation of stress with time where both parameters are expressed as their natural logarithms; i. e. ,

$$\ln stress = \quad _l \, \ln time \tag{5}$$

This form of the equation is shown for TP-H8278 aged for 36 weeks at $145°$ and $165°F$ on Figures 65 through 68. Note that in equation (4) the mechanical property is directly related to time with the coefficients in the equation having been determined from the infrared spectral information. This equation for mechanical properties can be used to predict properties at some future time based on the chemistry of aging as identified by the FTIS.

A relationship as shown in equation (2) can also involve more than one peak, resulting in a multiple correlation. Using stress as an example, the equation has the following form:

$$f(stress) = b_0 + b_1 f(P_1) + b_2 f(P_2) + b_3 f(P_3) \text{ ---- } + b_n f(P_n) \tag{6}$$

where P_1, P_2, P_3, etc. are the magnitudes of individual peaks. Equation (6) can also be used to predict other propellant mechanical properties by writing an equation for each peak height as a function of time, similar to equation (1). These equations relating peak height to time must exist for each of the peaks involved in equation (6). Using these individual equations relating peak height and time, one can then compute the magnitudes of all the peaks in equation (6) from their individual time-related equations for some future time period. These values then may be substituted into equation (6) and the mechanical property stress of the propellant calculated for the same future time used to calculate the peak heights.

This multiple correlation approach seemed an excellent way to arrive at a prediction capability, primarily because experience had shown that multiple correlations had a higher correlation coefficient than did the simple correlations. This fact infers that the chemistry of aging is not a simple zero-order or first-order reaction but that it involves several reactions, each proceeding at a specific rate. Prediction equations of this multiple correlation type were not calculated principally because time/peak height change correlations were not found for an entire group of peaks

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TP-H8278/W-65
Aged to 36 Weeks at 145° F

Modulus = $1233 (t)^{0.1478}$
r = 0.9696
r^2 = 0.9401
CV = 4.35%
Confid. lvl. = 99.9%

Time (Weeks)

Modulus, psi
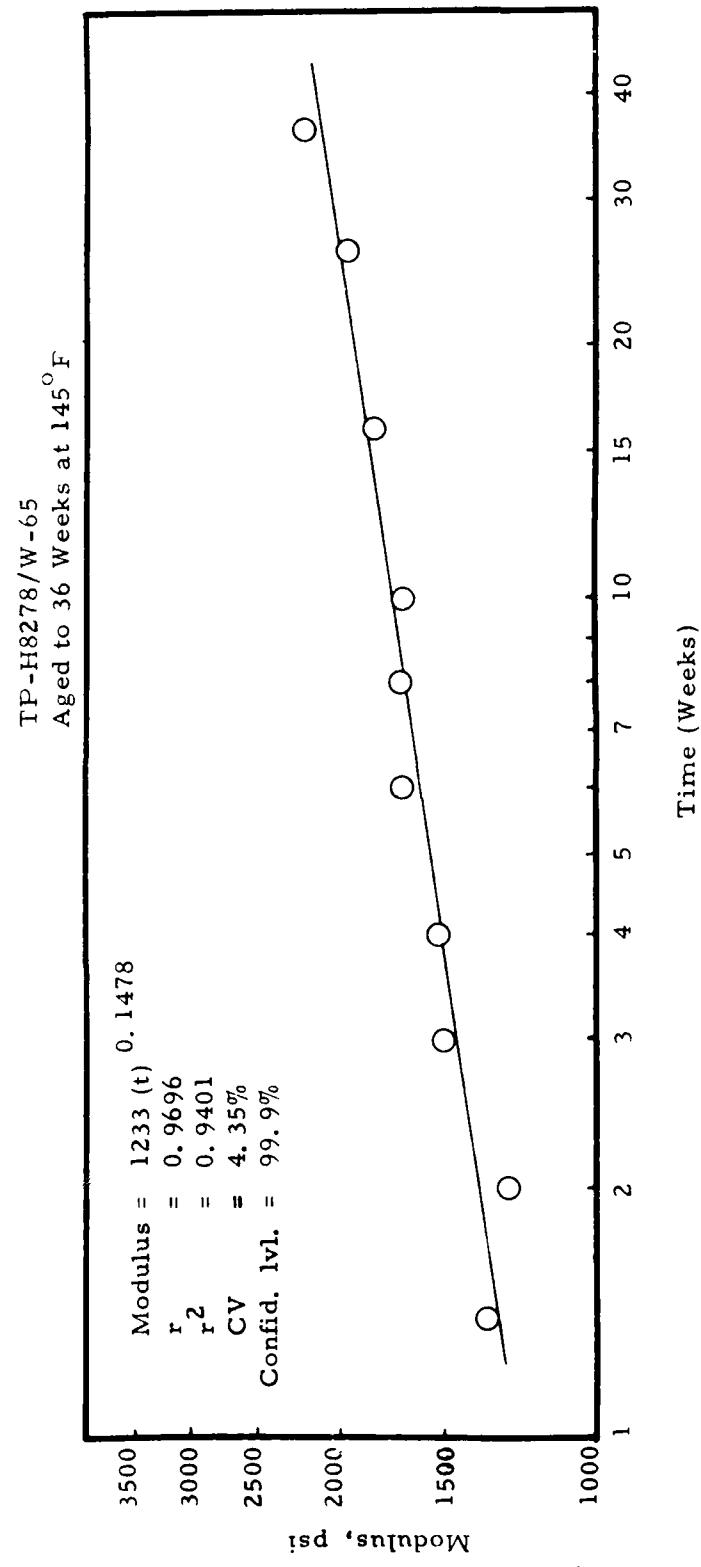
Figure 65. Relationship of Modulus and Time for 145° F Aging

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TP-H8278/W-65
Aged to 36 Weeks at 145°F

Stress   = 134.7 (t) $^{0.1094}$
r = 0.9729
r^2 = 0.9466
CV   = 3.01%
Confid. lvl. = 99.9%

Figure 66.   Relationship of Stress and Time for 145°F Aging

TP-H8278/W-65
Aged to 36 Weeks at 165° F

$$Modulus = 1379 \, (t)^{0.1519}$$
$$r = 0.9413$$
$$r^2 = 0.8861$$
$$CV = 6.41\%$$
$$Confid. \; lvl. = 99.9\%$$
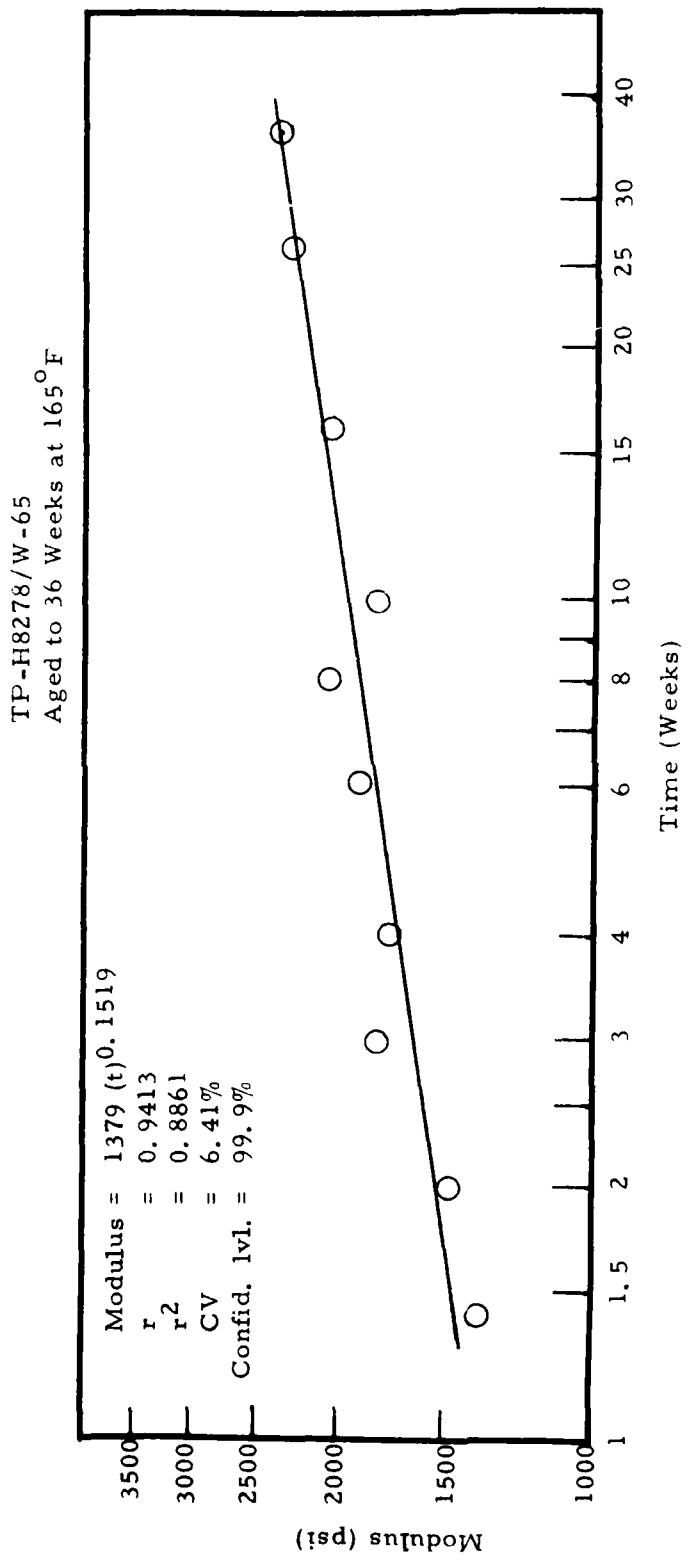
Figure 67.   Relationship of Modulus and Time for 165° F Aging

TP-H8278/W-65
Aged to 36 Weeks at 165° F

Stress = 151.3 (t) $^{0.0961}$
r^2 = 0.9354
r^2 = 0.8750
CV = 4.24%
Confiden. lvl. = 99.9%

Time (Weeks)

Stress (psi)
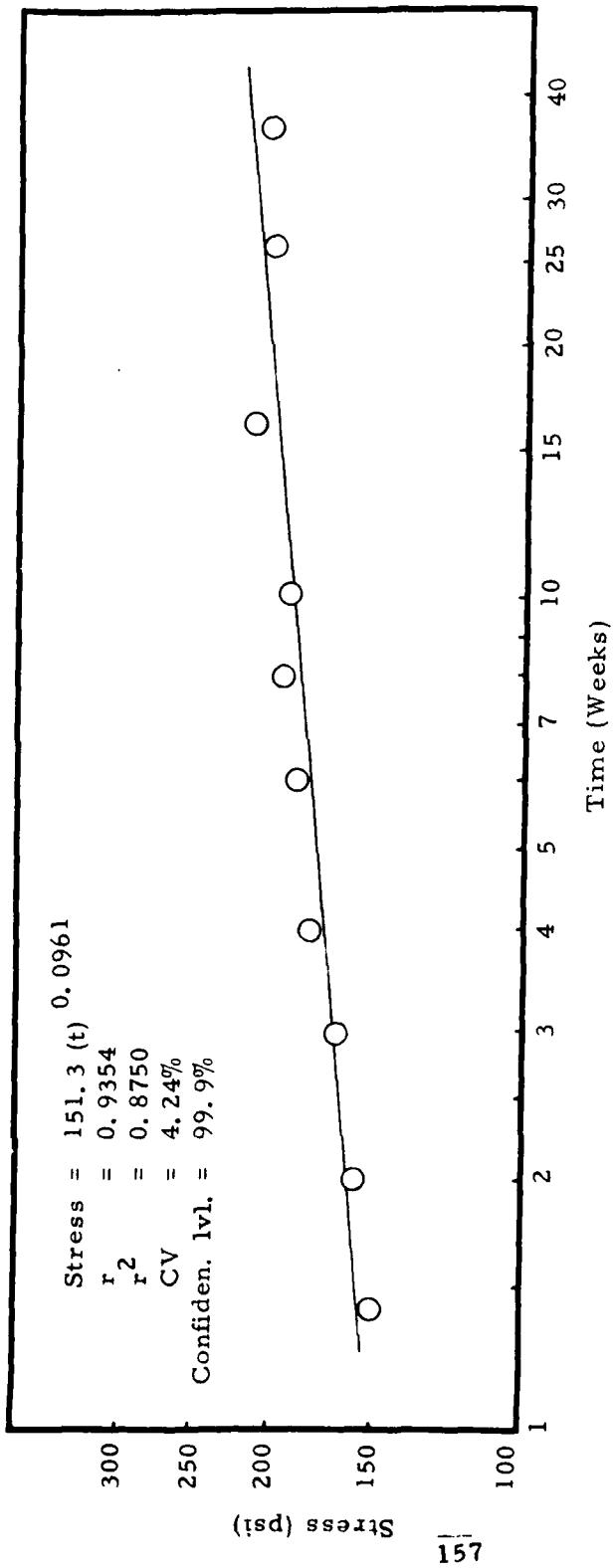
Figure 68. Relationship of Stress and Time for 165° F Aging

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describing a mechanical property change in the propellants examined. In several trials to derive a prediction equation, two out of three peaks appearing in an equation like (6) above would have a strong time correlation, but the third did not. Therefore, in order to demonstrate that the mechanical property prediction scheme was viable, we concentrated on finding **relationships** that involved only a single peak.

Correlations of these types were sought using the infrared spectra that had been accumulated during the project ... in particular, spectra for TP-H8278 propellant (the first propellant aged on the project) and TP-H8156. In the infrared data reduction and statistical analysis program (E490), time was added as a dependent variable so that time was correlated with the various peak height changes as well as propellant modulus, strain, and stress.

Correlations found for TP-H8278 propellant aged to 36 weeks at 165°F are presented in Table 35. There are two peaks in the infrared spectrum of the aged propellant whose height changes can be correlated with changes in propellant properties and with time. These peaks occur at 1514 cm^{-1} and 1236 cm^{-1}. The correlations in the case of the 1514 peak were greater for the mechanical properties than for time, and just the reverse was true for the correlations concerning the peak at 1236 cm^{-1}. No other time-base correlations were found; however, these two peak heights did give us an opportunity to test the prediction technique.

Spectra of propellant TP-H8156 aged at three temperatures, 130°, 170°, and 190°F, were examined for possible correlations of peak height changes with mechanical properties and with time. These data are presented in Table 36. At the 170° and 190°F aging temperatures, there is one point of commonality concerning the peaks that correlate with modulus, strain, stress, and time. That one peak occurs at 1708 cm^{-1} with the correlations at each of the aging temperatures being of approximately the same magnitude; however, it should be noted that at 190°F, the correlation of this peak with stress dropped out. At that temperature, there are strong correlations with modulus, strain, and time. At the 170°F aging temperature, there were strong correlations of that peak with modulus and stress and a slightly weaker correlation with strain, while the correlation with time was not as strong as the correlation had been at 190°F aging temperature.

TP-H8278 Propellant Aged 36 Weeks at 165°F

Working with TP-H8278 propellant, peak height at 1514 cm^{-1}, propellant stress, and time, an equation that would predict propellant stress based upon time was derived. The peak height at 1514 cm^{-1} correlated with stress, giving a correlation coefficient of -0.8875; and, from the peak

TABLE 35

SIMPLE LINEAR CORRELATIONS FOR

IR PEAK HEIGHTS/MECHANICAL PROPERTIES/TIME

(TP-H8278/W-65, Aged to 36 Weeks at 165°F)

	Dependent Variables			
IR Peak	Modulus	Strain	Stress	Time
1646 cm^{-1}	-0.7877		0.7630	
1514 cm^{-1}	-0.8387		-0.8875	-0.7444
1236 cm^{-1}	-0.7766	0.7111	-0.7594	-0.8427
965 cm^{-1}	0.7108	-0.8175		

NOTES:

1) Infrared peak height data are from the spectra of whole propellant.

2) Values shown in the table are the coefficients for correlations of the various IR peaks with propellant properties and aging time.

TABLE 36

SIMPLE LINEAR CORRELATIONS FOR
IR PEAK HEIGHT/MECHANICAL PROPERTIES/TIME

(TP-H8156/V6-13, Aged to 18 Months)

IR Peak	Dependent Variables				Age Temp.
	Modulus	Strain	Stress	Time	
3006 cm^{-1}	-0.7825			-0.9235	
2921 cm^{-1}			0.9072		190°F
1708 cm^{-1}	-0.9737	0.9089		-0.8317	
3006 cm^{-1}				-0.7234	
1708 cm^{-1}	-0.9658	0.8056	-0.9641	-0.7976	
1514 cm^{-1}	-0.9578	0.9217	-0.9008	-0.8085	
965 cm^{-1}	0.8439	-0.7261	0.7854		170°F
911 cm^{-1}	0.9472	-0.8190	0.8876		
526 cm^{-1}		0.7795			
679 cm^{-1}		0.8870			
718 cm^{-1}		0.8787		-0.7980	130°F
679 cm^{-1}		0.8864		-0.8512	

NOTES:

1) Infrared peak height data are from the spectra of whole propellant.

2) Values shown in the table are the coefficients for the correlations of the various IR peaks with propellant properties and aging time.

height data and stress data, the following equation was calculated by the least-squares method.

$$\text{Stress} = 605.7 - 166.7 \text{ (Peak Height at 1514)} \qquad (7)$$

Height of the peak at 1514 cm^{-1} correlated with time, giving a correlation coefficient of 0.7444; and, using the peak height data and time, the following equation was derived:

$$\text{Peak Height at 1514} = 2.661 - 0.0077 \text{ (Time)} \qquad (8)$$

A linear correlation of the peak height at 1514 cm^{-1} with time did not appear to be very good, so a correlation was made of the log of the peak height versus the log of time. This correlation, without the zero time data, gave a correlation coefficient of -0.8655 and the equation for the peak height had the following form:

$$\text{Peak Height at 1514} = 2.7173 \text{ (Time)}^{-0.0334} \qquad (9)$$

In order to have the peak height-versus-stress equation on the same basis as the log peak height/log time equation, it was necessary to drop the zero-time data and recalculate the equation for this relationship. This new relationship takes the form:

$$\text{Stress} = 575.9 - 154.6 \text{ (Peak Height at 1514)} \qquad (10)$$

This relationship had a correlation coefficient of -0.8366. An equation to predict stress, based solely on time, was derived by substituting equation (9) into equation (10) to give an equation having the following form:

$$\text{Stress} = 575.9 - 420 \text{ (Time)}^{-0.0334} \qquad (11)$$

Comparing the stress values calculated from equation (11) with the measured stress values gives a correlation coefficient of 0.9577.

Having derived an equation for stress based upon time, where the coefficients and exponents in the equation were derived solely from IR spectral data, it was then interesting to find the correlation between measured stress and time where the IR spectral information was not involved; two such equations were derived. The first, based on a linear relationship between stress and time, provided a correlation coefficient of 0.8346, not as good as the log/linear relationship derived from the infrared spectral information. The second equation involved the logarithm of stress and the logarithm of time and had the following form:

$$\text{Stress} = 148.0 \text{ (Time)}^{0.0990} \qquad (12)$$

This equation gave a correlation coefficient of 0.9578, a coefficient virtually identical to the one derived from the spectral information. A plot of equation (11) and equation (12) is given on Figure 69.

Using the approach described above, the same series of equations was computed for modulus. The relationship of the peak height at 1514 cm^{-1} and modulus had a correlation coefficient of -0.8387 and gave the equation:

$$Modulus = 9444 - 3007 \text{ (Peak Height at 1514)} \qquad (13)$$

The relationship of the peak height at 1514 and time had a correlation coefficient of -0.7444 and yielded the equation:

$$Peak \text{ Height at } 1514 = 2.661 - 0.0077 \text{ (Time)} \qquad (14)$$

Eliminating the zero-time test data so that the logarithmic relationship between peak height and time could be developed, the following equation was found:

$$Peak \text{ Height at } 1514 = 2.7173 \text{ (Time)}^{-0.0334} \qquad (15)$$

This correlation of the logarithm of peak height and the logarithm of time gave a correlation coefficient of -0.8655, better than the linear relationship between peak height and time. Recomputing the relationship between peak height and modulus while eliminating the zero time data gave the equation:

$$Modulus = 7888 - 2373 \text{ (Peak Height at 1514)} \qquad (16)$$

Now, substituting equation (15) into equation (16) gives the final equation for modulus, as follows:

$$Modulus = 7888 - 6448 \text{ (Time)}^{-0.0334} \qquad (17)$$

The correlation coefficient for measured-versus-computed modulus is 0.9798.

Derivation of the equation for the log of modulus versus the log of time using the mechanical property data and the test periods yielded the equation:

$$Modulus = 1287 \text{ (Time)}^{0.1666} \qquad (18)$$

On a log/log basis, the relationship between modulus and time had a correlation coefficient of 0.9900. This correlation coefficient is better than the one calculated using the infrared data only, but not by a large amount. Equation (17) and equation (18) are plotted on Figure 70. On a log/log plot, equation (18) is a straight line function, while equation (17) is curvilinear becaust it is a log/linear equation.

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TP-H8278/W-65, Aged 36 Weeks at 165°F

O - Measured Stress

Stress = 148(t)·⁰²⁹⁰
r = 0.9578

Stress = 575.9-420(t)⁻·⁰³³⁴
r = 0.9577

Time, Weeks

Stress, psi
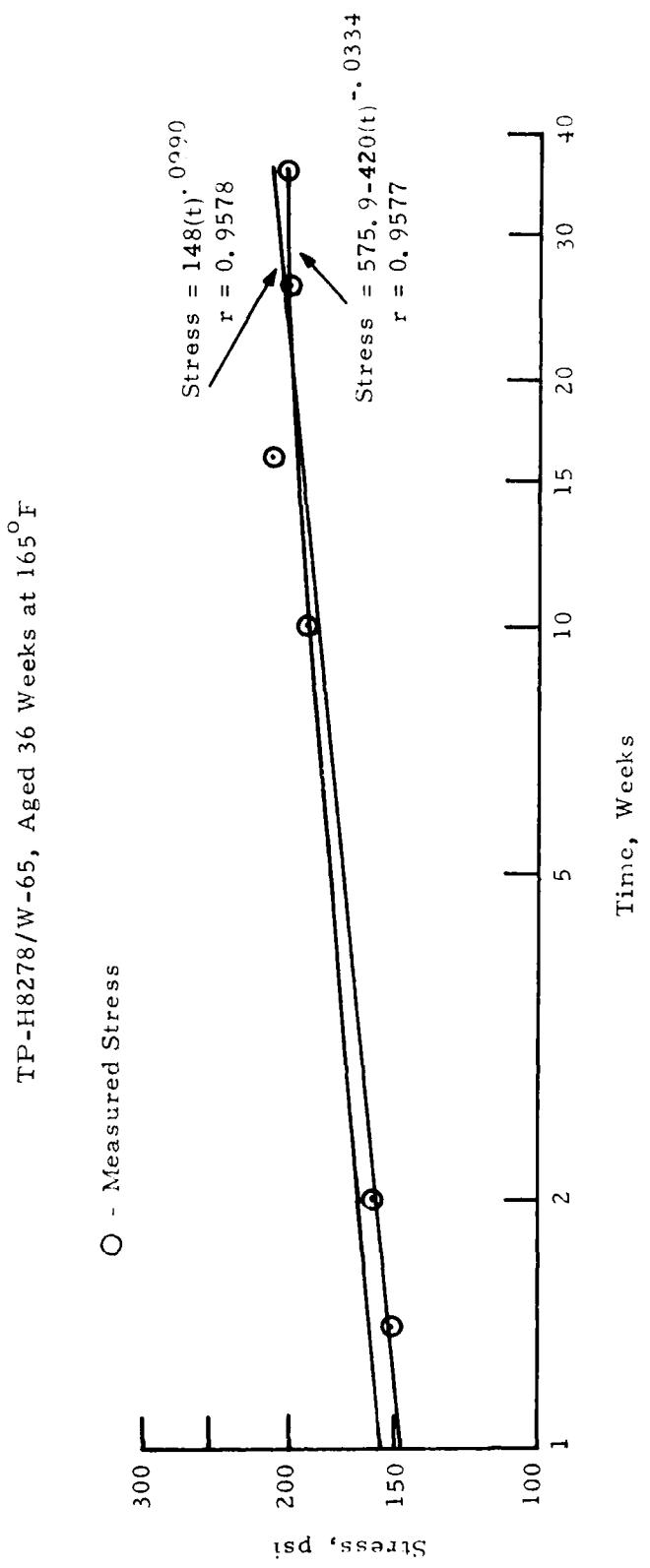
Figure 69. Equations for the Relationship of Stress and Time Show Strong Correlation with Measured Data.

TP-H8278/W-65, Aged 36 Weeks at 165°F

O - Measured Modulus

Modulus = 1287(t)·1666
r = 0.9900

Modulus = 7880-6448(t)−·0334
r = 0.9798

Time, Weeks

Modulus, psi
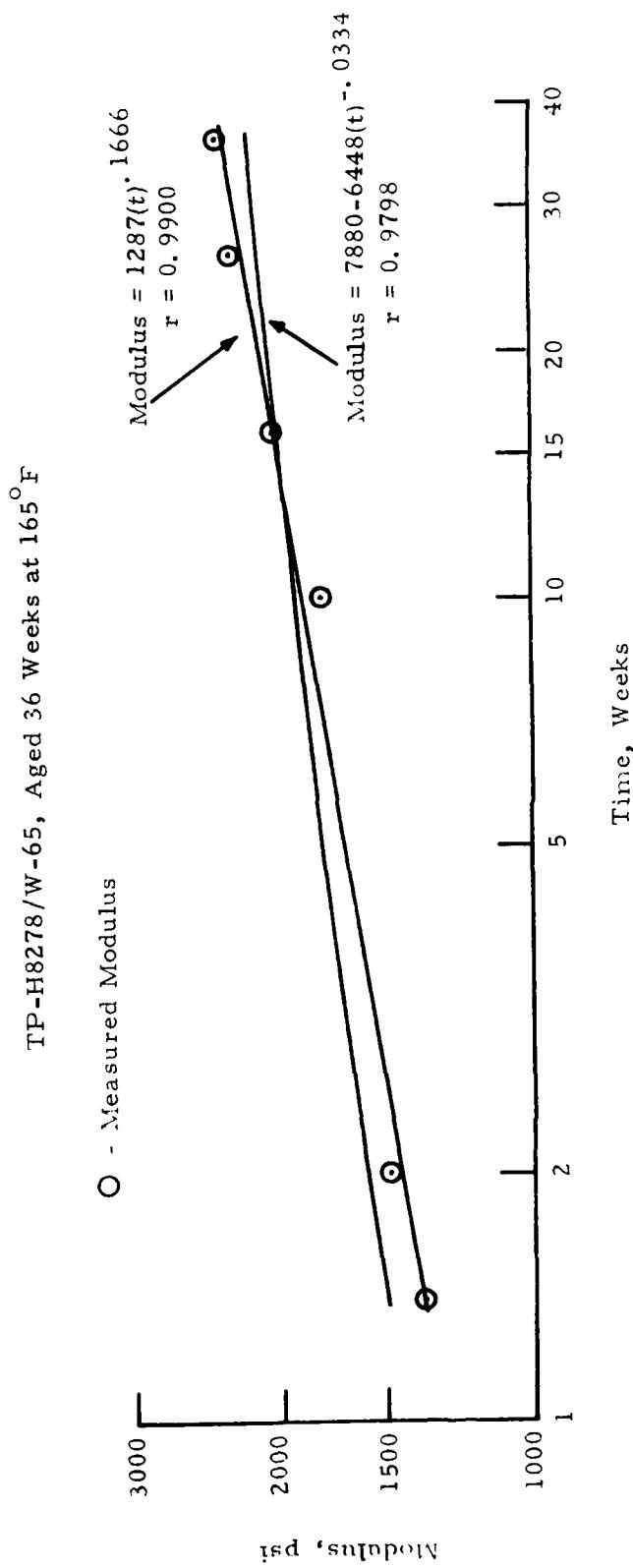
Figure 70. Equations for the Relationship of Modulus and Time Show Strong Correlation with Measured Data.

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TP-H8156 Propellant Aged 18 Months at 190°F

A similar set of equations was derived for TP-H8156 propellant that had been aged through 18 months at 190°F. The height of the peak at 1708 cm^{-1} was found to correlate with modulus on a linear basis with a correlation coefficient of -0.9737, while the correlation between peak height at 1708 and time on a linear basis was -0.8317. When this latter relationship was computed on a log/log basis, the correlation coefficient became -0.9572. Making the substitution of equations as described above yielded an equation for modulus based upon time, where coefficients and exponent were derived from IR data. It had the following form:

$$\text{Modulus} = 8492.9 - 6580.4 \,(\text{Time})^{-0.24013} \tag{19}$$

This relationship furnished a correlation with measured modulus of 0.9904. The correlation between the log modulus and log time, taking the measured modulus with its time of measurement, provided a correlation coefficient of 0.9337. Thus, in this instance, the equation for modulus derived from the infrared spectral information provided better correlation than did the relationship between modulus and time derived solely from the measured tensile data. This equation had the following form:

$$\text{Modulus} = 1881.5(t)^{0.4054} \tag{20}$$

These two equations are plotted on Figure 71.

Propellant TP-H8156 that had been aged at 170°F for 18 months also showed a strong correlation between modulus and the height of the peak at 1708 cm^{-1}. Equations as described above were calculated for the relationship between modulus, time, and peak height; these yielded a modulus equation based on infrared spectral data having the following form:

$$\text{Modulus} = 10721 - 9759 \,(\text{Time})^{-0.1288} \tag{21}$$

The correlation coefficient for calculated and measured modulus was 0.8886. When measured modulus and time were correlated, an equation having the following form was found:

$$\text{Modulus} = 1114.3 \,(\text{Time})^{0.4805} \tag{22}$$

The correlation coefficient for this was 0.9201. Here the equation based on measured modulus data provided better correlation than did the equation calculated from infrared spectral information. These two equations are plotted on Figure 72.
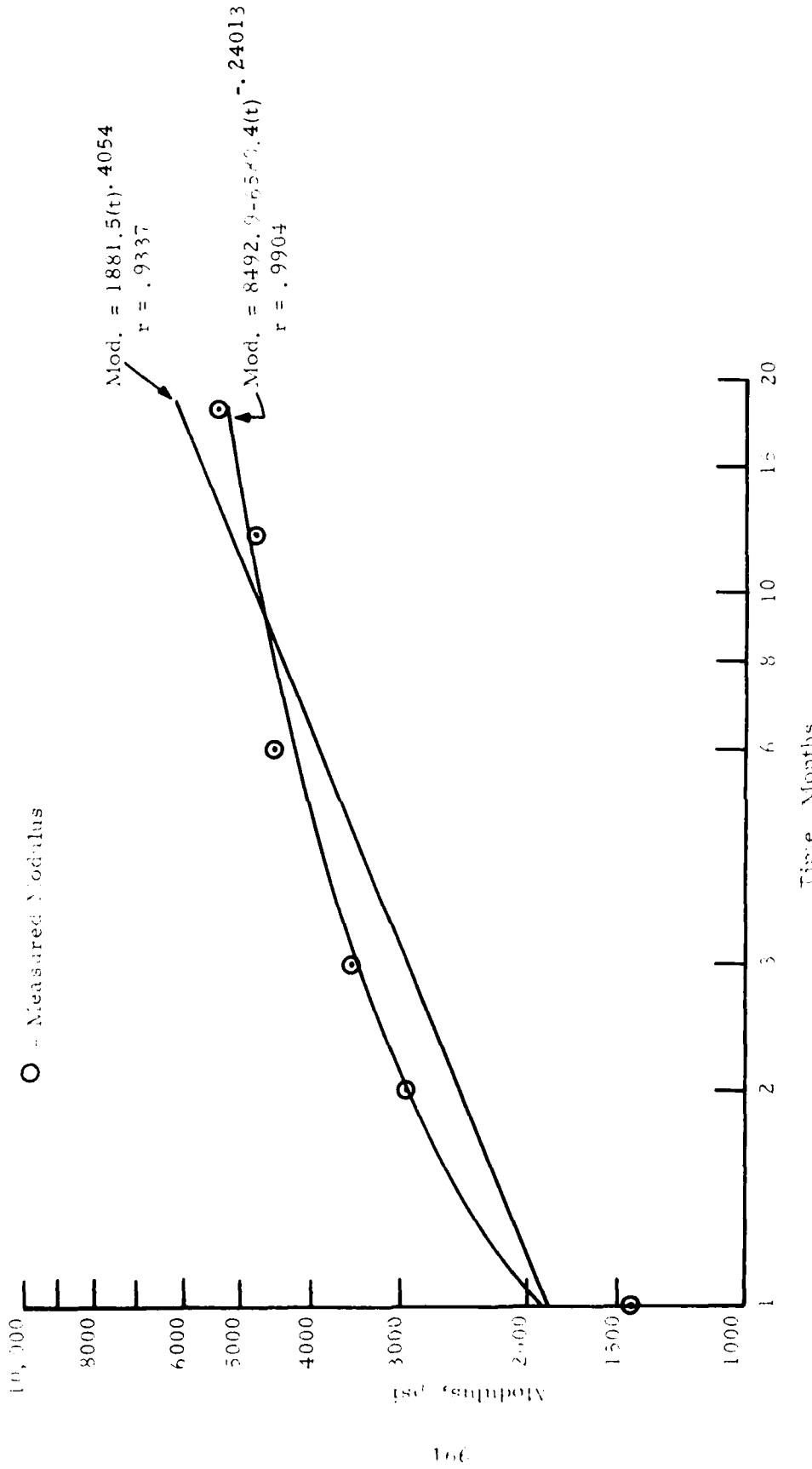
Figure 71. Equations for the Relationship of Modulus and Time Show Strong Correlation with Measured Data.

TP-H6Ì5ö/Vo-1ö, Aged 18 Months at 160°F

O - Measured Modulus

Mod. = 1881.5(t)·4054
r = .9337

Mod. = 8492.9-6547.4(t)^-.24013
r = .9904

Modulus, psi

10,000
8000
6000
5000
4000
3000
2000
1500
1000

Time, Months

1   2   3   6   8   10   15   20

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TP-H8156/V6-13, Aged 18 Mo. at 170°F

O - Measured Modulus

Modulus = 1114.3(t)$^{.4305}$
r = .9201

Modulus = 10,721-9750(t)$^{-.1288}$
r = .8886

Time, Months

Modulus, psi
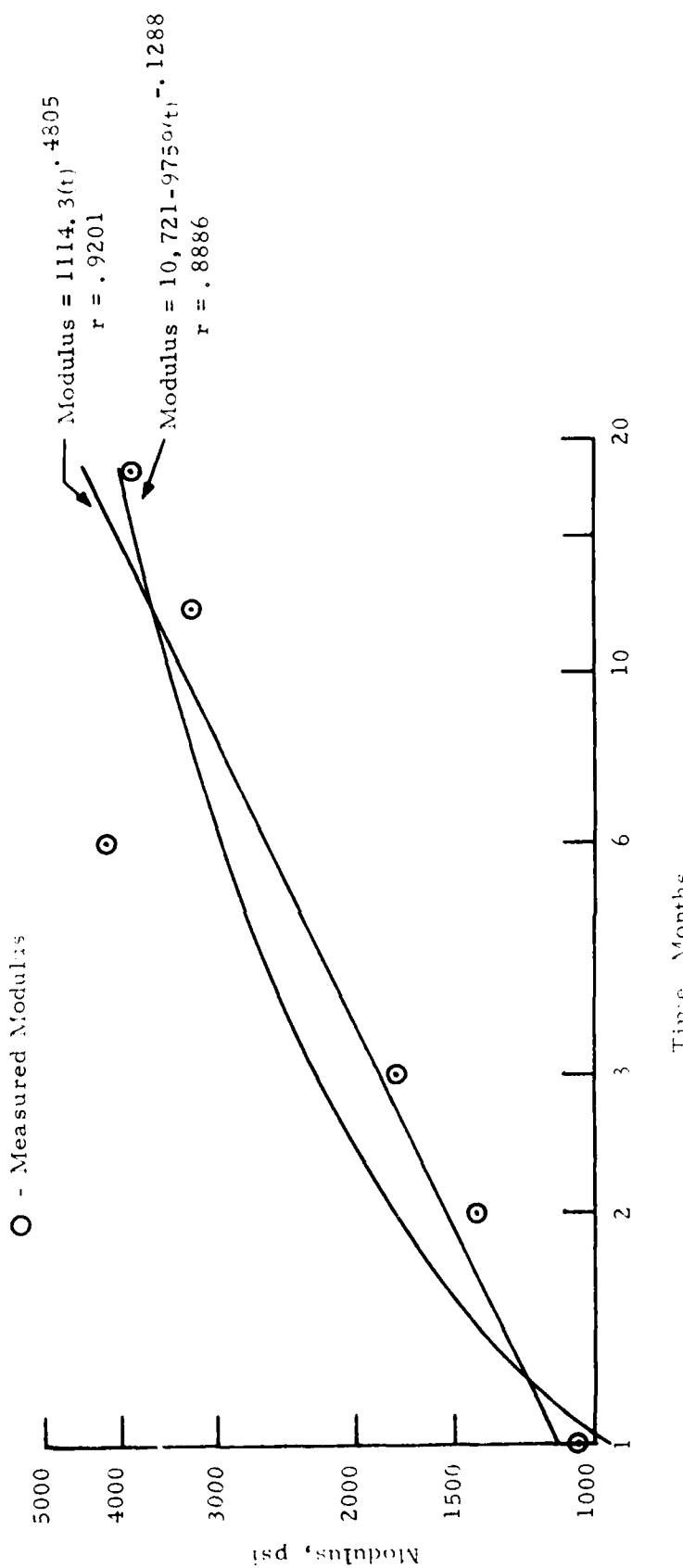
Figure 72. Equations for the Relationship of Modulus and Time Show Strong Correlation with Measured Data.

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Prediction of 52-Week Aging for TP-H8278

Using equation (17) for modulus and equation (11) for stress, we pre-
dicted the modulus and stress of the propellant at 52 weeks fo aging at 165°F.
Substituting "52" into the modulus and stress equations for the time factor,
at 52 weeks of aging, the modulus of the propellant was predicted to be 2237
psi and the stress 208 psi. The outcome of this prediction is shown in Table
37. The infrared-data-based equation for stress furnished a closer predic-
tion than did the equation describing the stress/time relationship. Just the
opposite was true for modulus. Here the modulus/time equation provided a
closer prediction. Those predictions are considered to be good, especially
for modulus. Since modulus is not a directly measureable property, its
prediction would be difficult under the best of circumstances.

Prediction of 24 Weeks Aging for TP-H8156

Using equations (19), (20), (21), and (22), predictions were made for
the modulus of TP-H8156 after 24 months of aging at 170° and 190°F. These
predictions along with the measured data are shown in Table 38. Here the
IR-data-based equations provided a more accurate prediction than did the
modulus/time based equation. Comments, made above, concerning prediction
of a derived value rather than a measured value are equally valid here.

The mathematical approach to prediction of propellant properties to a
future time using infrared spectral data has been shown to be viable and to be
at least as accurate, if not more so, than a prediction based upon the history
of the change in a property with time.

Computer Programs at AFRPL

The development of Computer Programs E-410 and E-490 is described
under Phase I in this report. The programs accomplish the computerized
reduction and statistical analysis of infrared data from the FTS-10 spectro-
photometer. These codes were first programmed for use on the IBM 370
computer at Thiokol's Huntsville Division. After they were made operational
on that computer, they were programmed for use on CDC 6600 computers.
When this additional programming was completed, the programs were made
operational on the CDC 6600 computer at AFRPL. During installation of the
programs on the CDC 6600 computer, card decks and a user's manual for
the programs were delivered to AFRPL. The remote computer terminal at
Thiokol could communicate directly with the AFRPL computer, and it was
used extensively during adaptation of the programs for the CDC 6600 com-
puter. As a final step, however, Thiokol's principal investigator and com-
puter programmer visited AFRPL during October 23-25, 1979 to assure that
the programs worked properly on the AFRPL computer. Satisfactory operation
of the programs and understanding were confirmed by the proper solution of
test problems that were supplied.

TABLE 37

PREDICTED AND MEASURED PROPERTIES OF

TP-H8278 AFTER 52 WEEKS AT 165°F

	Measured Value	Predicted by IR Based Equation	Predicted by Time/ Property Equation
Stress, psi	203	208[a]	218[c]
Modulus, psi	2662	2237[b]	2486[d]

---

[a] Predicted using equation (11).

[b] Predicted using equation (17).

[c] Predicted using equation (12).

[d] Predicted using equation (18).

TABLE 38

PREDICTED AND MEASURED MODULUS OF

TP-H8156 AFTER 24 MONTHS at 170° AND 190°F

	Measured Value	Predicted by IR Based Equation	Predicted by Time/ Modulus Equation
Modulus, 190°F	4482	5425[a]	6824[c]
Modulus, 170°F	3406	4240[b]	5131[d]

---

[a] Predicted using equation (19).

[b] Predicted using equation (21).

[c] Predicted using equation (20).

[d] Predicted using equation (22).

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CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Conclusions presented here are major project conclusions which are related to the project objective and show that the object was reached. Conclusions concerning individual facets of the project are given at the end of appropriate sections in the main body of the report.

1) IR spectra of solid propellant made by the ATR technique are quantitative.

2) IR spectral changes in solid propellant correlate with propellant mechanical property changes, using IR spectra made from whole propellant, AP-leached propellant, propellant binder sol fraction and propellant binder gel fraction.

3) Correlation among spectral peak height changes and propellant mechanical property changes, where age-time is a constant and age-temperature a variable, can be used to identify the mechanical properties of a propellant where the aging conditions of the propellant are unknown.

4) Mechanical properties of solid propellant can be predicted to a future time using a mathematical equation where the constants, coefficients, and exponents of the equation are derived from IR spectral data.

RECOMMENDATIONS

1) Include FTIS-aging technology as a part of major solid propellant aging programs so that mechanical property identification and prediction capability will be available when the propellant reaches field-use.

2) Employ the current state-of-the-art of FTIS technology to determine the age life of field-stored rocket motors.

3) Develop a technique for taking a "non-destructive" sample of the propellant in a field-stored rocket motor so that the properties of the propellant can be identified for service-life prediction.

4) Develop a technique for taking the IR spectrum of propellant within a rocket motor without removing a sample, i. e. , field inspection employing a technique such as IR emission spectroscopy.

5) Conduct tests to provide statistical confirmation of the correlations between IR spectral changes and propellant mechanical property changes.

GLOSSARY

Amplitude — absorbance (or transmittance) value at any given point on an infrared spectrum.

ATR — Attenuated Total Reflectance. A technique and apparatus for obtaining IR spectra of opaque materials.

Baseline — an imaginary line representing the appearance of a spectrum if a peak were not present.

BPA — bis phenol A diglycidyl ether

FFP — Frequency of the First Point. A spectral wave number value determined by the FTS-10 computer based on the user selected STP (starting point) of the IR spectrum.

FLP — Frequency of the Last Point. A spectral wave number value determined by the FTS-10 computer based on the user selected ENP (ending point) of the IR spectrum.

FTIS — Fourier Transform Infrared Spectroscope

FTS-10 — A single beam infrared spectrophotometer manufactured by Digilab, Inc., Cambridge, Mass.

IRE — Internal Reflection Element. A truncated prism which is the sampling optical element in an ATR unit.

Irtran 4 — A material used to make IR windows and IRE's chemically it is zinc selenide (Zn Se).

KRS-5 — A material used to make IR windows and IRE's. It is thallium bromideiodide.

Peak height — the maximum amplitude of a spectral peak minus the baseline amplitude at the same wave number.

Resolution Element — $\text{Resolution Element} = \dfrac{FFP - FLP}{\text{No. of Data Words}}$

Wave Number — the reciprocal of IR wave length, the unit of measure is reciprocal centimeters (cm^{-1})

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APPENDIX A - SAMPLE PREPARATION

Samples of propellant used in the FTIS analyses, the ammonium perchlorate leaching tests and the gel/sol separation came from between the JANNAF specimens that were cut for tensile testing the propellant. These "islands" of propellant offered several advantages. Principally, they represented waste propellant and the composition of the propellant at that point should be identical with the composition of the propellant that was actually tensile tested. If there is to be a correlation between infrared spectral information and propellant mechanical properties using propellant adjacent to the tensile specimens themselves offers the best possibility of finding such a correlation. Using these "islands" offered another advantage in that the physical dimensions of the small pieces of propellant were almost precisely the size required for the ATR unit used in the greater part of the studies; i.e., the Barnes Engineering Company ATR unit.

Preparation of samples for FTIS analysis required only that the propellant be cut into thin slides using a microtome. Propellant was cut to thicknesses of approximately 0.020 inch. The actual thickness was found to be non-critical so long as it was in the region of 0.015 to 0.030 inch. Samples thinner than 0.015 inch were too difficult to handle and samples thicker than 0.030 inch presented some difficulties in the ATR unit, principally in getting the sample pressed firmly and flat against the ATR prism. After cutting the thin slivers of propellant, they were stored in a metal can and sealed to prevent contact with moisture and to prevent free exchange of air inside the can with air outside the can. Samples were then stored in a freezer at approximately -20°F so that there would be little or no change in the chemistry of the sample. This was done purely as a convenience and offered an opportunity to rerun samples at a later time.

Figure A-1 is a sketch showing the area from which the propellant samples were taken. The crosshatched area represents the samples that were used for various analyses. The block of propellant shown on Figure A-1 is a 0.5-inch-thick slice taken from a standard 1/2-gallon ice cream carton. The 1/2-gallon carton is a standard sample cast for the purpose of making tensile specimens and for aging programs. The broken tensile specimens themselves could be used for the FTIS analysis, provided the ATR unit employed does not use more than a 0.4 inch of propellant. The ATR unit employed in this study (Barnes Engineering Company) needed a sample that was approximately 0.55 inch, therefore, the width of the broken tensile specimens was not great enough to fill the surface of the IRE employed in the ATR unit. The sample size for the Harrick ATR unit is 4 mm by 50 mm so that the tensile specimens themselves could be microtomed for the FTIS analysis, provided there was a single section of the broken tensile specimen 50 mm in length.

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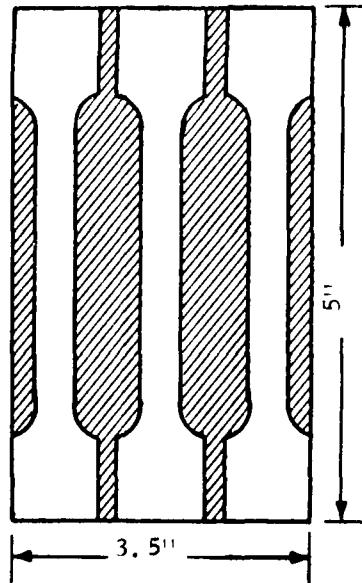
Figure A-1. Scrap Propellant Between Tensile Specimens Is Used For
FTIS Analysis.

APPENDIX B - AMMONIUM PERCHLORATE LEACHING

Removing ammonium perchlorate from samples of propellant prepared as described in Appendix A was most conveniently accomplished using a constant-temperature water bath containing about 7.5 gallons of water. The water bath was maintained at a temperature between 35° and 40°C and was stirred constantly. Samples of the propellant were suspended in the bath by means of small clamps and a suitable ring stand support for the clamps so that the entire sample of propellant was submerged in the water. The bottom of each sample of propellant was weighted to prevent it from floating to the surface of the water with the weight arranged such that it clamped across the width of the propellant to also prevent the propellant sample from curling later during the drying process. "Bobby pins" were found to be a very useful low-cost weight with reasonable rust resistance. The weight of one or two bobby pins was found to be sufficient to hold the sample underneath the water and prevent it from floating up and sufficiently strong to clamp across the width of the propellant to prevent it from curling.

During washing the samples absorb water and grow to be approximately twice their dry volume. During the drying process, the samples shrink to approximately their original size.

A sample thickness of 0.020 inch was found to be ideal for the AP leaching. Samples much thinner than this were too fragile to handle when they became saturated with water, and would very easily break from the weight attached to the bottom of the sample. Samples much thicker than this were found to require excessively long times to remove all of the ammonium perchlorate from the sample. Using a sample of 0.020 inch thickness, the ammonium perchlorate was removed in about 24 hours.

The following procedure was used to test for the presence of ammonium perchlorate. A sample was removed from the water bath and rinsed with distilled water. The surface of the sample was blotted dry with a paper towel and the sample thus dried was transferred to a watch glass. A small amount of internal water was pressed from the swelled sample onto a watch glass and the sample was returned to the water bath. The watch glass, with the sample of internal water, was placed in an oven and the water evaporated; the watch glass was then inspected for the presence of a white crystalline solid. If there was solid present, the washing was continued; if there was no solid on the watch glass, all AP had been removed from the sample and the set of samples were then placed in an oven for drying.

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After all of the AP had been leached from the propellant sample
samples were dried still attached to the clamps and with the weights in
place. They were positioned so that they hung vertically in an oven at
60°C. About 4 hours was required to remove the majority of the water
drying was continued then at room temperature overnight.

Because the propellant samples after leaching the ammonium
perchlorate were used for the infrared analysis, it was important that t
samples remain flat so that they could be properly positioned and press
firmly against the IRE of the ATR unit. The tendency of a sample to cu
during drying was found to be inversely proportional to the sample thick
This is one reason for selecting a sample of about 0.020 inch in thicknes
The leaching time was found to be directly proportional to sample thick
and inversely proportional to ammonium perchlorate particle size. The
propellants containing a large percentage of very small particle ammon
perchlorate were found to take longer than 24 hours to remove all of the
ammonium perchlorate. Based on these observations concerning leach
time and the tendency of the sample to curl, even with a clamp across
the bottom of the sample, a sample thickness of 0.015 inch and a maxin
sample thickness of 0.020 inch was found to present the fewest number
problems in leaching.

Infrared spectra of whole propellant, ammonium perchlorate leached propellant and propellant gel fraction were obtained using the following standard procedure.

The Barnes Engineering Company ATR unit requires two samples, one for each face of the internal reflection element (IRE). One sample is 12 mm x 14 mm, the other is 22 mm x 14 mm. These samples are positioned on the appropriate side of the IRE and the sample retaining plates, or pressure plates, are positioned and the bolts holding the pressure plates to the sample are tightened finger tight. Bolts are then tightened with a torque screwdriver to the required level. The torquing is done in small increments in a crossing pattern to assure that the pressure plates remain flat and parallel to the surfaces of the IRE. The amount of torque required is a function of the modulus of the propellant, the higher the modulus, the more torque required to obtain a spectrum of "reasonable" magnitude.

Where whole propellant is used as the sample, the maximum absorptive value in the spectrum should lie between 80 and 130 absorption units. Where the propellant sample has had the ammonium perchlorate leached, the maximum absorptive value in the spectrum should lie between 50 and 100 absorptive units. In the case of whole propellant, the largest peak in the spectrum will occur at approximately 1040 cm^{-1} and this is the dominant peak in the ATR absorption spectrum of ammonium perchlorate. The organic proportions of the propellant spectrum will be at considerably lesser values. Having the absorption of the peak at 1040 cm^{-1} lying between 80 and 130 absorptive units means that the maximum absorption of the organic portion of the spectrum will lie in the region of 20 to 40 absorptive units, which places the organic materials in a region where the information is quantitative.

Using the Barnes ATR unit, experience has shown that it is not necessary to exceed a torque level of 40 oz-in to achieve a spectrum of the proper magnitude.

The Harrick Scientific Corporation ATR unit requires two specimens approximately 4 mm x 50 mm. These are placed on either side of the IRE and are held in place by two pressure plates which are tightened by a single bolt. This single bolt should be tightened slowly, using a torque screwdriver, to the maximum peak height specifications described above for the Barnes ATR unit.

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In assembling the ATR units, one should always be aware of the hardness value of the IRE being used, and the torque on the assembly bolts limited so as to not deform the IRE. KRS-5 is fairly soft and can be deformed by single large crystals of ammonium perchlorate if the pressure becomes excessive. Hardness values of the three IRE materials evaluated in the project are listed below. The numerical value assigned to hardness is based upon sodium chloride having a hardness of 1.

KRS-5	=	2.2
Irtran 4	=	8.3
Germanium	=	160.0

After having obtained the infrared spectrum of the propellant, the IRE's are washed with methylene chloride and rinsed with ethanol to remove moisture condensed by the rapid evaporation of the methylene chloride. It is important that the IRE's be washed thoroughly to remove all traces of organic material left by the sample of propellant.

If in assembling the ATR units a sample is "over-torqued", i.e., the maximum absorptive value in the spectrum exceeds the values quoted above, it will be necessary to disassemble the ATR unit, remove the sample of propellant, wash the IRE, and use a fresh sample of propellant. The reason for this is, if the specified absorptive values exceed the values quoted above, the spectrum may not be in the linear quantitative region and the comparison of one specimen with another would not produce valid data. A fresh sample must be used simply because the process of applying pressure to the propellant squeezes some of the sol material out of the specimen and deposits it on the surface of the IRE.

In taking the ATR spectrum of propellant, the following FTS-10 collect parameters are used. Some of these parameters control the amount of information allocated to a file and, since the computer program has been designed to accept a file size of 468 data words or less, it is important that the selection of these collect parameters be such that the specified file size is not exceeded. The following parameters were used throughout the program. Parameters marked with an asterisk are those which control the file size.

DPM = P
GRR = -1
NSS = 250
*RES = 8
SEN = 4
*UDR = 2
*WDS = SP
*ZFF = 1
*STP = 400 cm^{-1}
*ENP = 400 cm^{-1}

The parameter DPM (double precision mode) governs how much of the interferrogram is collected in double precision and how much is collected in single precision. It was the practice that this parameter be set to P (partial). There is no harm in setting the parameter at F (full). The value P is sufficient so long as NSS is not so large as to cause a data overflow in the FTS-10 computer. If a large number of scans (>400) are to be collected, then DPM should be set to F.

The value GRR (gain ranging radius) was normally set to -1, and found no occasion to use any other value.

The parameter NSS was set for 250, and we found that the co-addition of 250 scans of a single sample was sufficient for an adequate signal-to-noise ratio. The larger NSS, the better the signal-to-noise ratio, and the better the quality of the spectra.

RES (resolution) was set to 8; and, since this is one of the parameters which controls file size, it is recommended that a resolution of 8 be used.

The parameter SEN (sensitivity) was set to 4 simply because this is normally the largest value that can be used without getting an A/D overflow error message. SEN should be set as large as possible because this parameter affects the singal-to-noise ratio, and a large SEN improves the quality of the spectra.

UDR is the under sampling ratio, and is also another parameter which controls file size. The value of this parameter should not be altered without taking steps to limit the file size to 468 data words.

WDS (word size) governs whether the data collection is performed in single precision or double precision. We did not find it necessary to use a double precision collection, and so used single precision. This, again, is a parameter that controls file size and the single precision collection should not be changed without taking steps to limit file size to 468 data words.

ZFF (zero filling factor) was set to 1, and we found no advantage to using a value other than 1. It, too, is a file size controlling parameter, and should not be changed without taking steps by adjusting other parameters so that the file size does not exceed 468 data words.

The values STP (starting point) and ENP (ending point) should be set to 4000 and 400, respectively. These values control the computer set parameters FFP and FLP (under circumstances where UDR is greater than 0). These values, FFP and FLP, are used along with file size (the number of data words in an FTS file) to calculate the resolution element for each FTS file.

In collecting a reference file (RFL) for use in computing a spectrum, the collection parameters shown for a sample file (SFL) should also be used. The parameter SEN will, of necessity, be smaller than the value used for an SFL.

Work during the program revealed the necessity for some ground rules concerning the ATR unit used in accumulating the IR spectral data. In order to have the IR spectral data reproducible and of good quality, we found that the following parameters must be held constant throughout an entire aging program:

1) The ATR apparatus used must be the same.

2) The angle of incidence of the IR energy on the internal reflection element must be held constant.

3) The material from which the internal reflection element is made and the entrance aperture angle must also remain constant.

APPENDIX D - GEL/SOL SEPARATION

Separation of the gel fraction and the sol fraction of the binder from the propellant is accomplished using methylene chloride in a Soxhlet extraction apparatus. For gel fraction separation, a sample of propellant from which the ammonium perchlorate had been leached was positioned in the extraction chamber of a Soxhlet apparatus such that the sample was hanging vertically and was constrained at its lower end so that the sample could not curl or otherwise change its shape during the extraction process. Extraction of the sol fraction and all other soluble materials, from the sample of propellant, took approximately 24 hours using methylene chloride as the extracting solvent. The temperature of the propellant never exceeded 40°C so that there were few, if an, changes in the chemical composition of the sample because of heat.

After the extraction had been completed, the sample was withdrawn and hung vertically in an oven at 60°C for 1 hour to remove all traces of the methylene chloride. The sample consisting of the gel fraction of the binder plus those water and methylene chloride insoluble solids was then used for infrared spectral examination.

Where it was desired to test the sol fraction of the propellant, approximately 5 grams of propellant cut on a microtome into very thin slices (about 0.005 inch), were placed into a ceramic thimble and the thimble placed in the Soxhlet apparatus. The propellant was extracted with methylene chloride for 24 hours. The sol fraction plus those methylene chloride-soluble ingredients in the propellant were recovered from the solvent flask of the apparatus by evaporation of the methylene chloride. The dried sol fraction, a liquid, was then used for the infrared examination.

APPENDIX E

AP-LEACHING EXPERIMENTS

In examining the spectra of whole propellant and spectra of propellant where AP had been leached out by water in some early experiments, a slight change in the amplitude of the peak at 1713 cm^{-1} was observed. These spectra were made from slices of the same piece of propellant. A close inspection of other regions of the spectra revealed differences elsewhere; but the peak at 1713 cm^{-1} was noticeably smaller in the ammonium perchlorate-leached propellant. From this we must conclude that there are low molecular weight, organic species being washed from the propellant along with the ammonium perchlorate. This does not mean that leaching AP from propellant is not a useful technique for removing the spectral influence of ammonium perchlorate so that more of the organic peaks in the IR spectrum can be examined. It does mean, however, that there may not be correlations between AP-leached propellant and whole propellant. There may be correlations between AP-leached propellant and mechanical properties that are or are not present in the spectrum of the whole propellant.

As a result of making this observation, several experiments were run to confirm the usefulness of leaching ammonium perchlorate from propellant. Having the computer program for IR data reduction available meant that a large number of propellant samples could be examined so that the repeatability of the IR data/mechanical property correlations could be identified.

Experiments that were run were as follows:

Experiment A - Ammonium perchlorate was leached from several series of TP-H8156 propellant samples. These samples had been aged 0 to 12 months at 75°, 110°, 130°, 150°, 170°, and 190°F. The ammonium perchlorate leaching procedure was to submerge all samples from a particular aging temperature in a trough of running water at 35° to 40°C for periods from 22 to 24 hours or until the ammonium perchlorate had been removed. These samples were then dried in an oven at 55° to 60°C for 4 hours and then overnight at room temperature. Infrared spectra of all propellant samples, 43 samples, were run.

Experiment B - The infrared data accumulated on each of the unleached samples used in "A" above was accumulated and reduced by the computer. These IR spectra were the ones originally run at the time that the samples were originally tested; i.e., for the "0" time spectrum, a one-year old spectrum was used, for the one-month aging samples, 11-month old spectral data was used, so that the spectra employed in this experiment were the original ones.

DATA CORRELATIONS FOR AP-LEACHED PROPELLANT (Experiment A)

As with all previous sets of spectra data, where we looked for correlations between spectral changes and mechanical property changes in propellant, if there are no mechanical property changes (or if those mechanical property changes are very slight), then we would not expect to see propellant spectral changes. There were no strong correlations found with propellant aged at 75°F.

With propellant aged at 110°F, a correlation was found with the spectral peak located at 912 cm^{-1}. There are some data scatter as can be seen in Figure E-1. This scatter can be either mechanical property data scatter (strain at maximum stress) or it can be relative peak height scatter.

Propellant aged at 130°F showed a correlation between strain at maximum stress and the peak at 912 cm^{-1}. There also appeared to be a correlation with the peak at 1739 cm^{-1} and this same mechanical property although it was not nearly as strong as the correlation with the peak at 912 cm^{-1}. Correlations are plotted on Figure E-2.

Propellant aged at 150°F in this series did not reveal any strong correlations between infrared spectral data and propellant mechanical properties.

Several strong correlations were observed for propellant aged at 170°F. These correlations are displayed in Figures E-3, E-4 and E-5. The correlation between maximum stress and the peak at 1738 cm^{-1} is a fairly strong one, particularly if the same assumption is made concerning error in measurement of maximum stress. This same peak also correlated well with modulus provided the same assumption was made concerning error in the measurement of modulus. A correlation also appeared to be present between strain at maximum stress and the peak located at 912 cm^{-1}. Correlations, although not as strong as it apparently was for the 110° and 130°F aging temperatures, does appear to hold for this higher temperature, 170°F aging also.

In the case of propellant aged at 190°F, there were several very strong correlations. These are shown in Figures E-6, E-7 and E-8. The peak at 1738 cm^{-1} correlated very well with propellant modulus. Again, we see a correlation with the peak at 912 cm^{-1}. This correlation being with strain at maximem stress. Changes in the peak at 1515 cm^{-1} show some correlation with maximum stress. An examination of that plot on Figure 16 reveals the possibility of two distinct lines - a lower one connecting the shorter age time points and an upper line connecting the three longer age time points. One could also draw a single line through all points and have a fairly good correlation. This correlation, however, is not exceedingly strong. Figure

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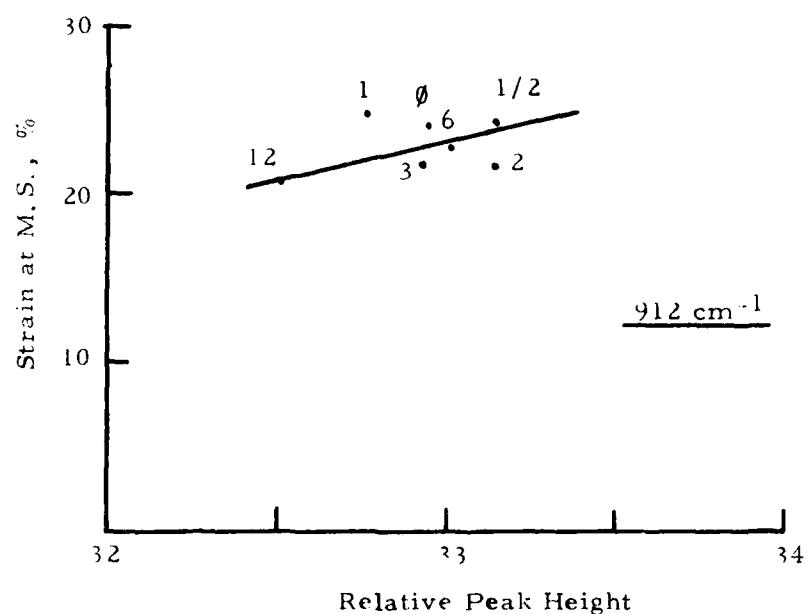
Figure E-1. Correlation of Peaks at 912 cm^{-1} and Strain.
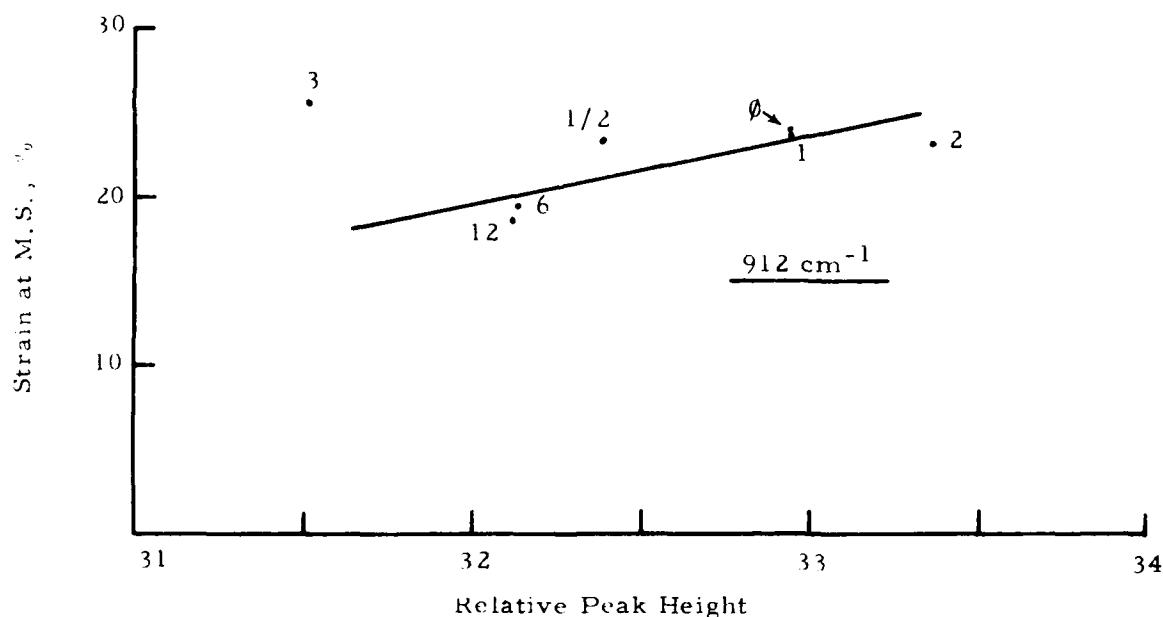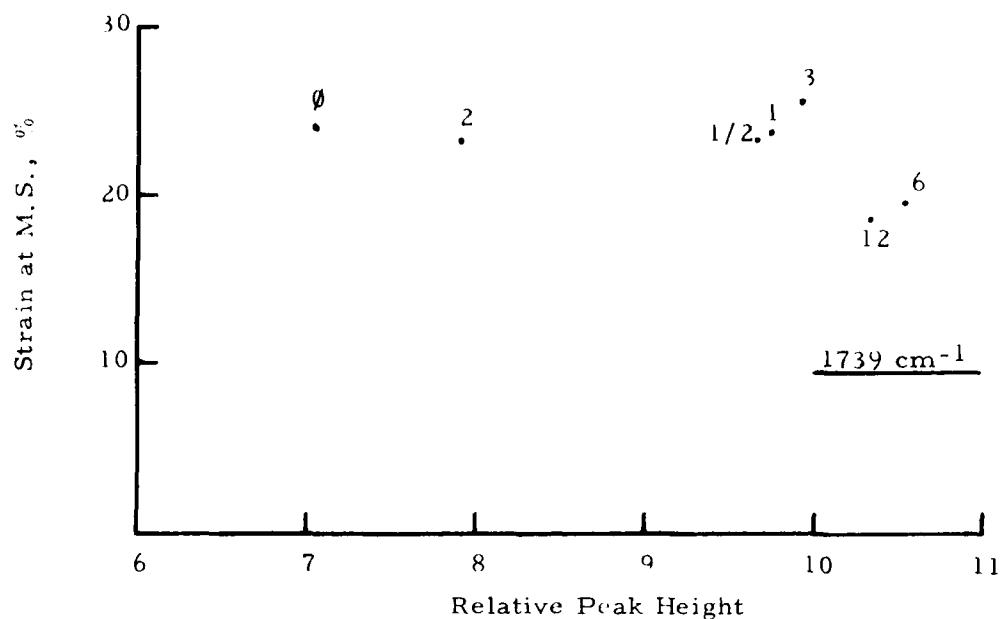
Figure E-2. Correlation of Peaks at 912 cm^{-1} and 1739 cm^{-1}, and Strain.

TP-H8156/V6-13 Aged 12 mo. at 170°F
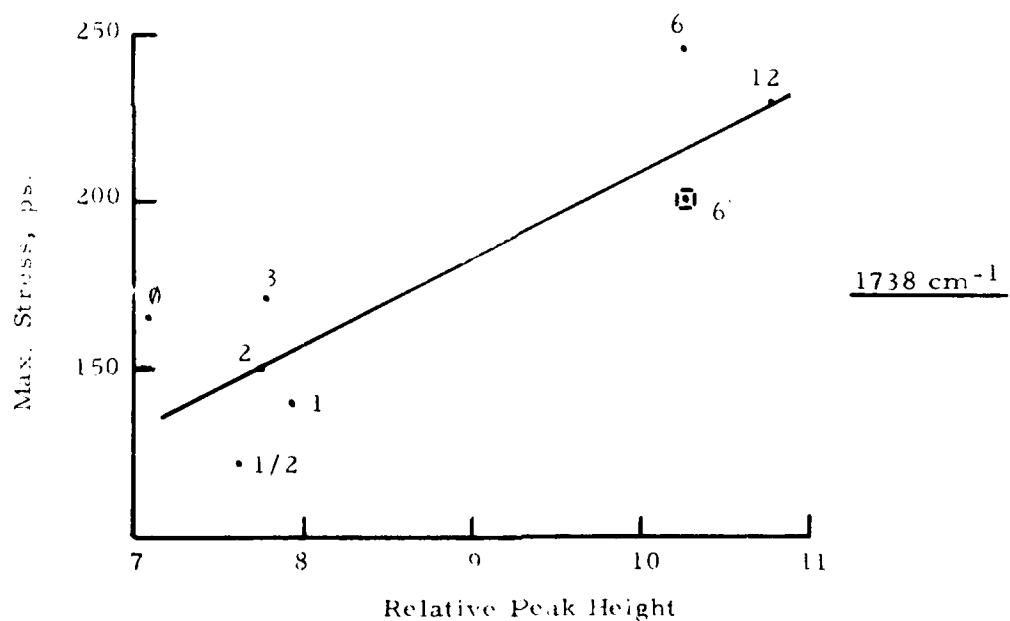
AP leached w/H₂O

Figure E-3. Correlation of Peak at 1738 cm⁻¹ and Stress.

TP-H8156/V6-13 Aged 12 mo. at 170°F
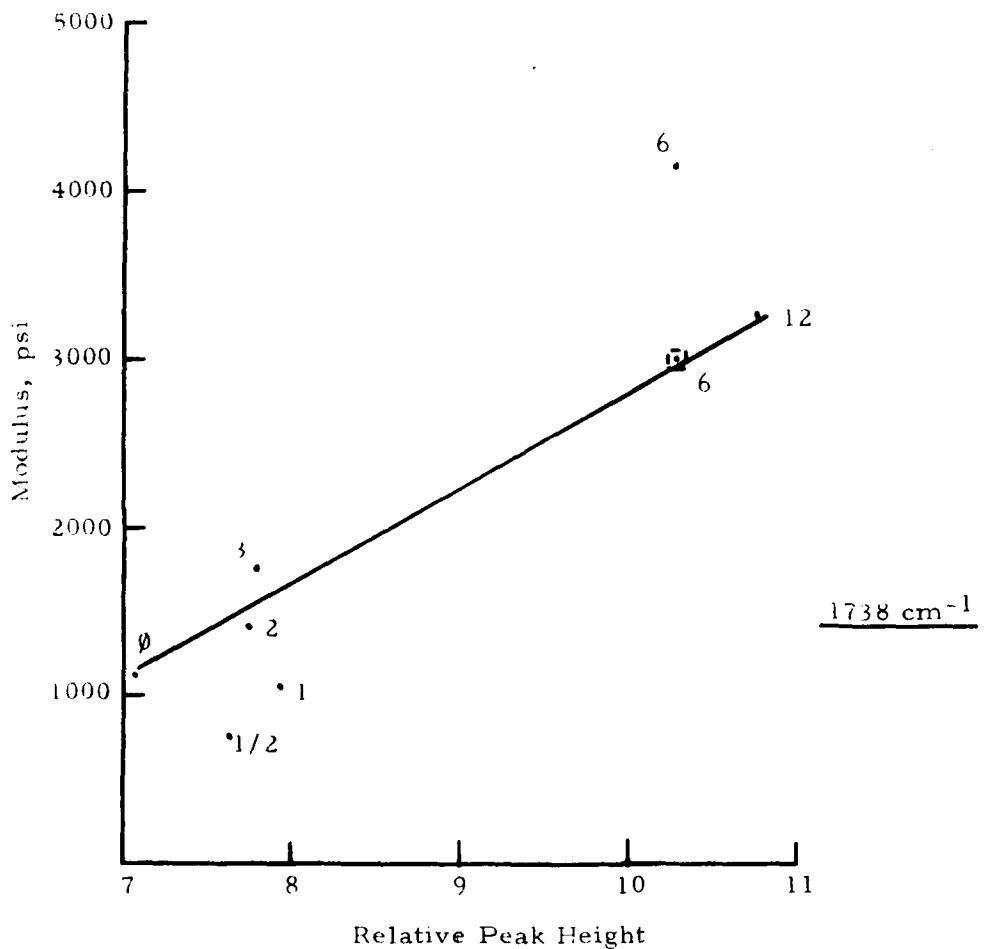
AP leached w/H_2O

Figure E-4. Correlation of Peak at 1738 cm^{-1} and Modulus.

TP-H8156/V6-13 Aged 12 mo. at 170°F
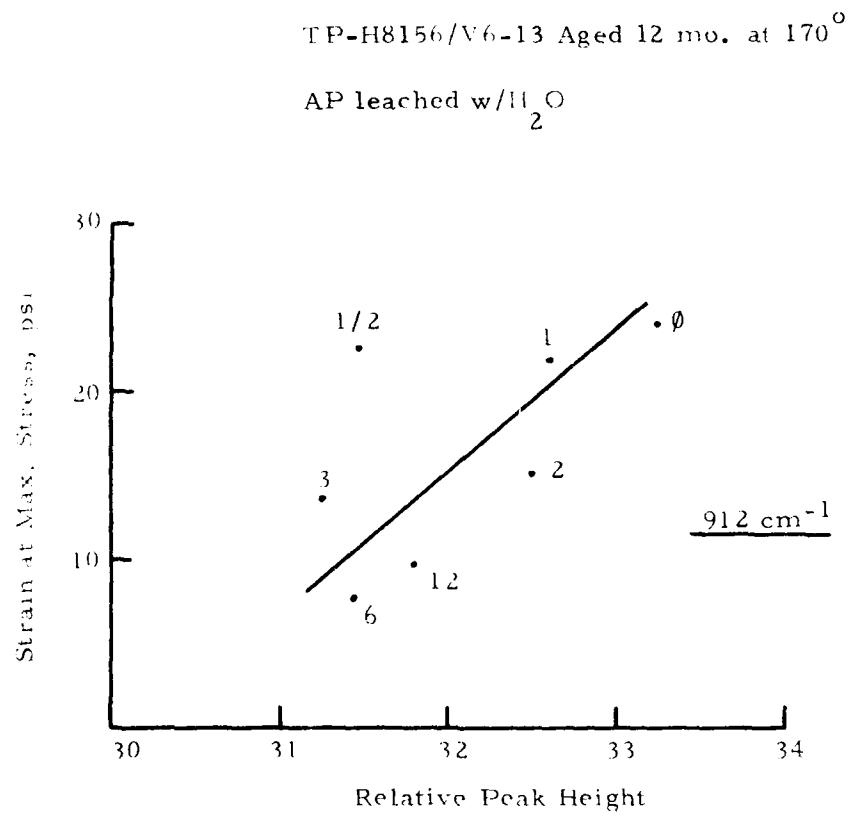
AP leached w/H_2O

Figure E-5. Correlation of Peak at 912 cm^{-1} and Strain.

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Figure E-6. Correlation of Peak at 1738 cm^{-1} and Modulus.
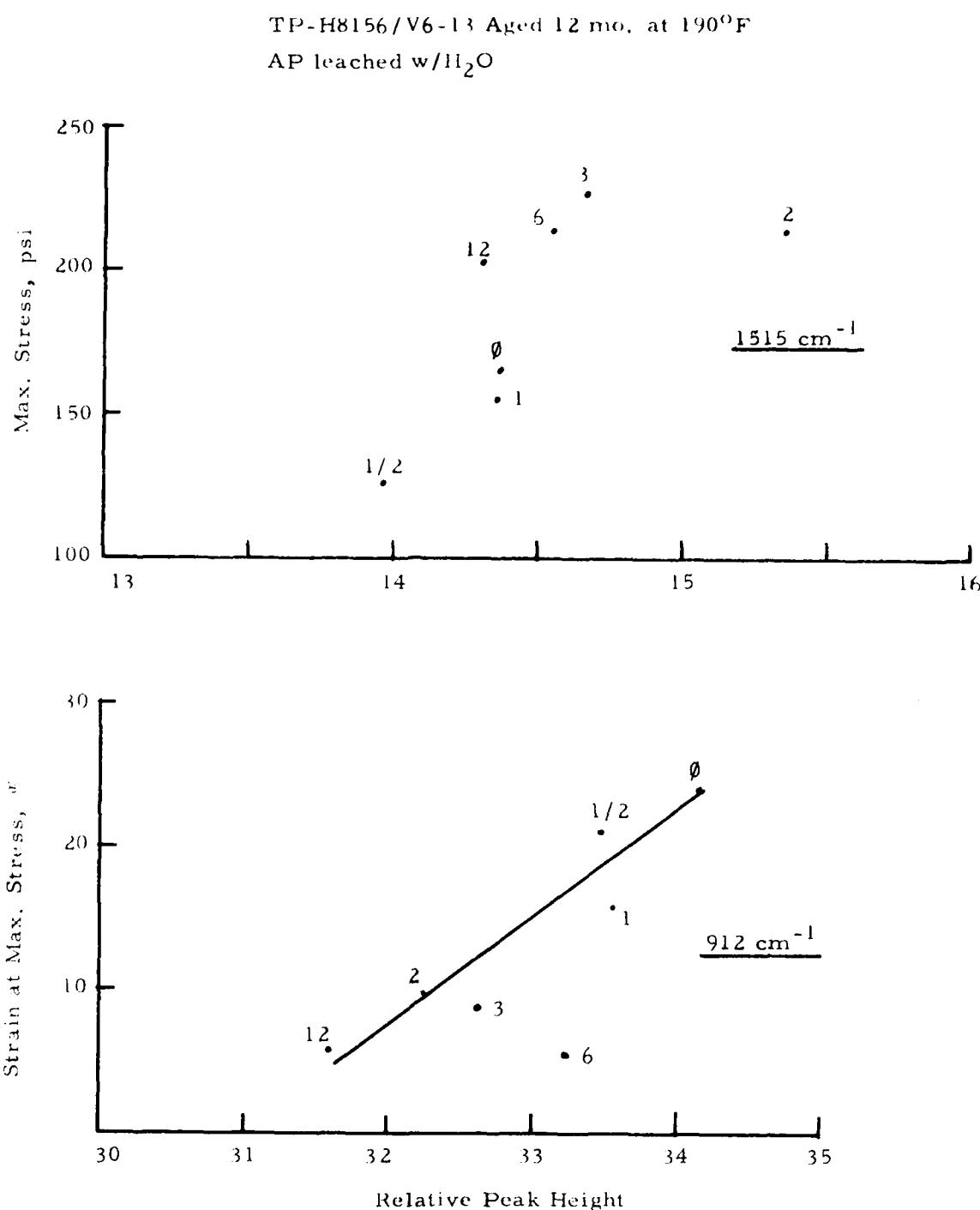
Figure E-7. Correlation of Peak at 912 cm^{-1}. Strain and Stress.

TP-H8156/V6-13 Aged 12 mo. at 190° F

AP leached w/H_2O
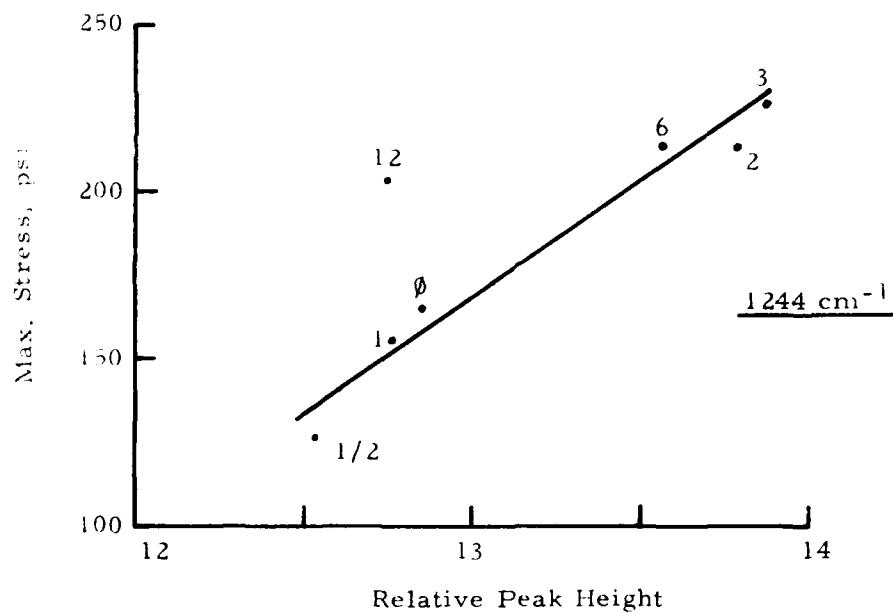
Figure E-8. Correlation of Peak at 1244 cm^{-1} and Stress.

E-8 reveals a very strong correlation of maximum stress changes with changes in the peak at 1244 cm^{-1}.

As was done for the infrared spectra of the whole propellant, we have taken spectra of the propellant from which ammonium perchlorate has been leached and we have plotted peak height change for various peaks where age time is a constant (12 months) and age temperature is one of the variables. A review of that data showed that there were three peaks whose changes could be correlated with changes in propellant mechanical properties. These peaks were located at 1734, 1437, and 912 cm^{-1}. Correlations occurring with the peak at 912 cm^{-1} are displayed on Figure E-9 and show some very strong relationships there. The relationship of the peak height changes at 1437 cm^{-1} were correlated with maximum stress; and, although there are two "outliers", the correlation certainly appears to be a valid one (see Figure E-10). Changes in the height of the peak at 1734 cm^{-1} correlated with both modulus and strain at maximum stress. These relationships are displayed on Figure E-11.

DATA CORRELATIONS FOR WHOLE PROPELLANT (Experiment B)

Because of the presence of ammonium perchlorate in the spectrum, the number of organic binder peaks that can be examined is greatly reduced. Particular attention was paid to peaks occurring at or near 1744, 1713, 1515, 1250, 965, 910, and 833 cm^{-1}.

Correlations at 1713 cm^{-1} and 1744 cm^{-1} for Propellant Aged at Constant Temperature

Data reduction was performed to examine the pair of peaks occurring at 1713 cm^{-1} and at 1744 cm^{-1}. Because these two small peaks are approximately the same magnitude, it was considered a better data reduction technique to treat them with a common baseline running from the minimum or tangency point on one side of the pair of peaks to the minimum or tangency point on the other side of the pair of peaks. Using this data reduction technique we were able to establish some very positive correlations of these two peaks with propellant mechanical properties with the quality of the correlation varying as a function of aging time and temperature.

A tabulation of the peak heights at 1713 and 1744 cm^{-1} versus age time for each of six age temperatures is presented in Table E-1. Plotting these two peaks against time revealed a curve shape that was distinctly similar to one or more of the mechanical properties plotted versus time. The graphs of these two peaks against time at the 190° and 170°F age temperature are shown in Figures E-12 and F-13, respectively. Mechanical property plots for the propellant aged at these temperatures are given on Figures E-14 and E-15. Neither of the peaks seem to correlate at all with strain, so the correlations

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TP-H8156/ V6-13 Aged 12 mo. at various temp.
AP leached from propellant
Normalized at 2920 cm^{-1}
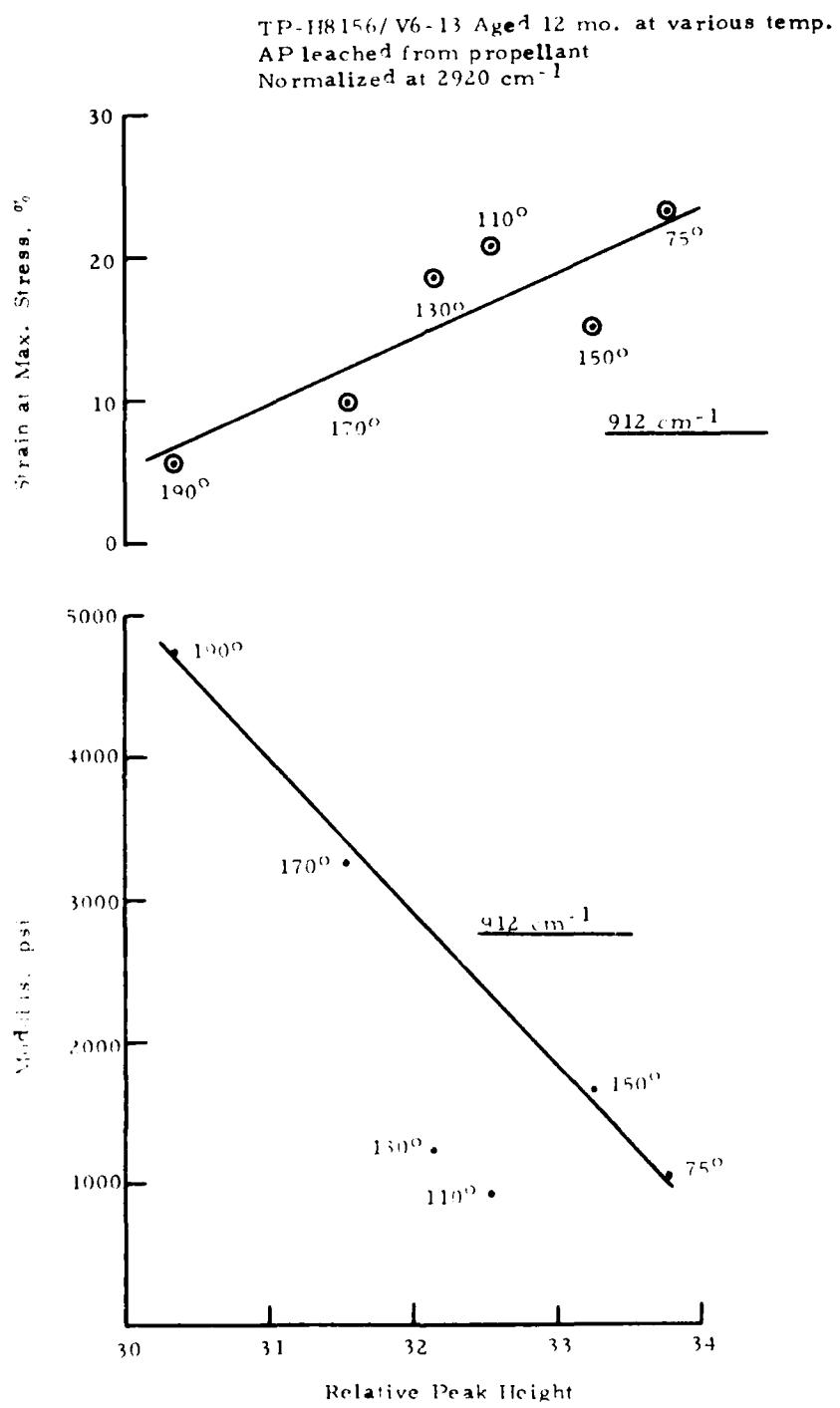
Figure E-9. Correlation of Peak at 912 cm^{-1}, Modulus and Strain.

TP-H8156/V6-13 aged 12 months
at various temperatures.
AP leached from propellant
Normalized at 2920 cm^{-1}
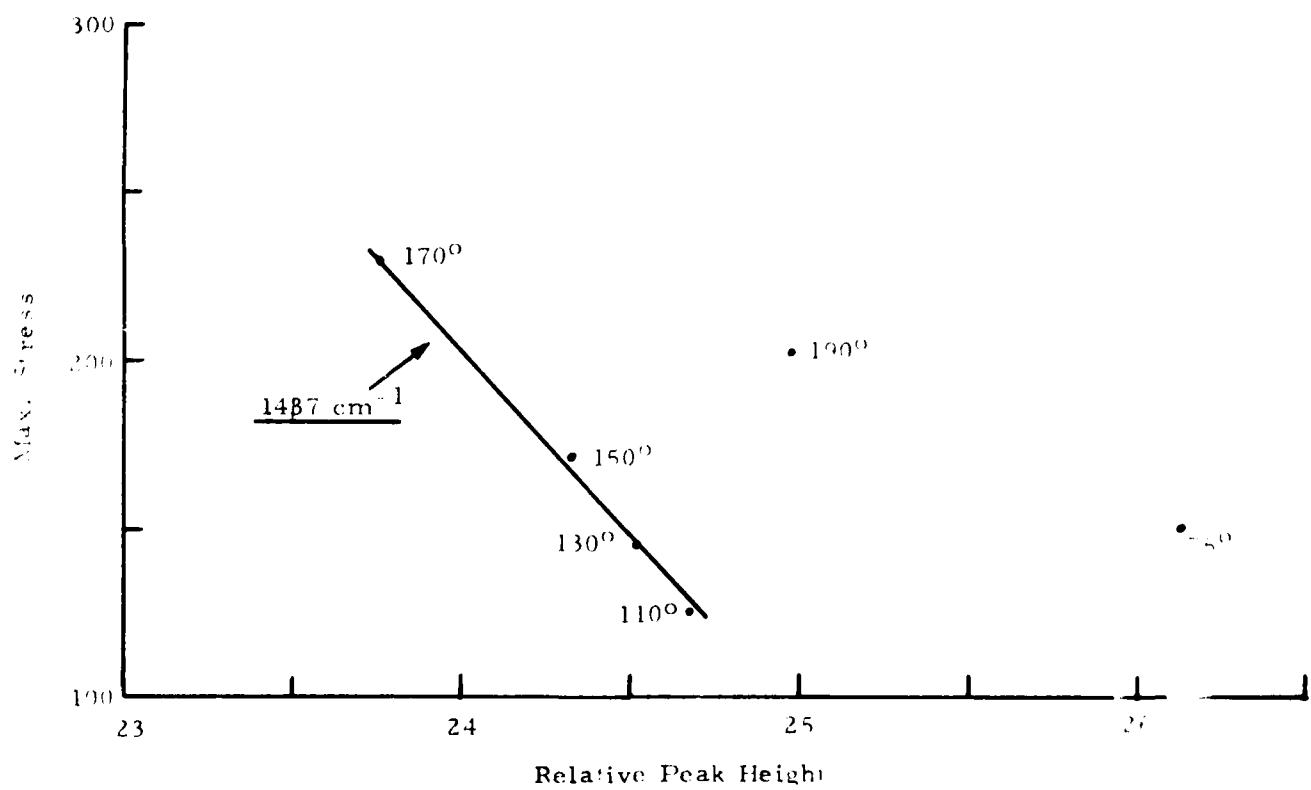
Figure E-10. Correlation of Peak at 1437 cm^{-1} and Strain.
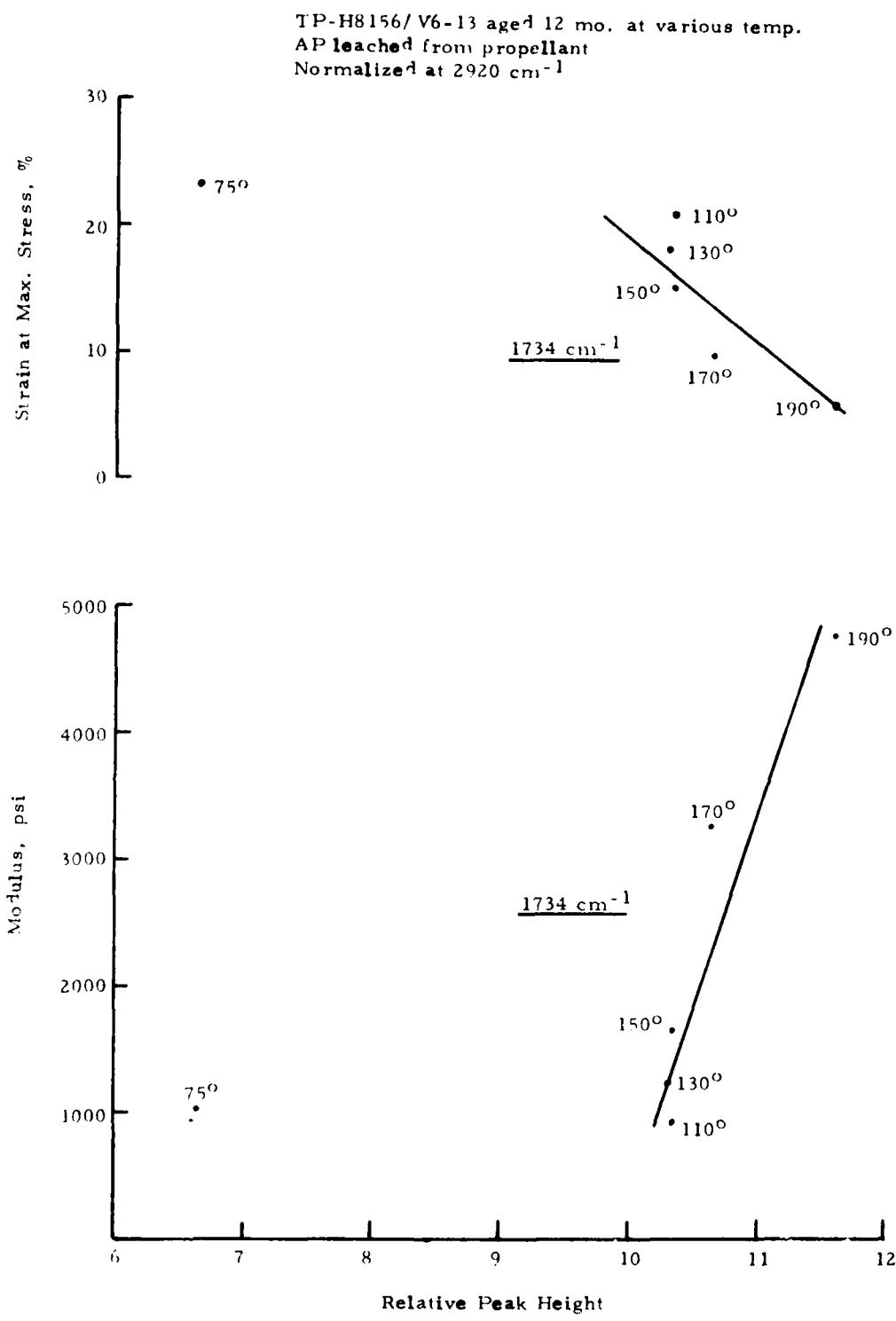
Figure E-11. Correlation of Peak at 1734 cm^{-1}, Modulus and Strain.

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TABLE E-1

TP-H8156/V6-13 AGED AT VARIOUS TEMPERATURES

Age Temp, °F	Wave No.	Age Time, Months						
		0	1/2	1	2	3	6	12
190	1744	4.02	3.51	3.87	3.64	3.591	3.462	3.195
	1713	4.16	4.73	3.89	2.817	2.693	1.998	1.427
170	1744	4.492	3.964	4.063	4.189	4.282	3.940	4.370
	1713	4.650	4.874	4.871	4.240	4.205	3.194	3.147
150	1744	4.900	4.527	4.446	4.565	4.301	5.203	4.901
	1713	5.072	5.166	5.294	4.742	4.893	5.236	4.598
130	1744	5.091	4.790	4.779	4.428	4.879	5.324	5.173
	1713	5.315	5.304	5.580	4.927	5.211	5.495	5.303
110	1744	5.553	5.127	5.347	5.111	5.456	5.902	5.192
	1713	5.748	5.180	6.129	5.442	5.490	5.987	5.337
75	1744	4.731	4.574	4.545	4.333	4.858	4.680	4.607
	1713	4.898	4.789	5.364	4.549	4.619	4.853	4.257

NOTES: (a) Spectra by Barnes ATR/KRS-5.

(b) Whole propellant, spectra taken immediately after tensile testing of propellant.

(c) Data reduced using common baseline for peaks at 1744 and 1713 cm^{-1}.

(d) Spectral information (amplitudes and W.N.) came from computer normalized data. Normalized at 2920 cm^{-1}.

Figure E-12.   IR Peak Height Changes With Time.

TP-H8156/V6-13
Aged at 170° F
Whole Propellant Spectral Data
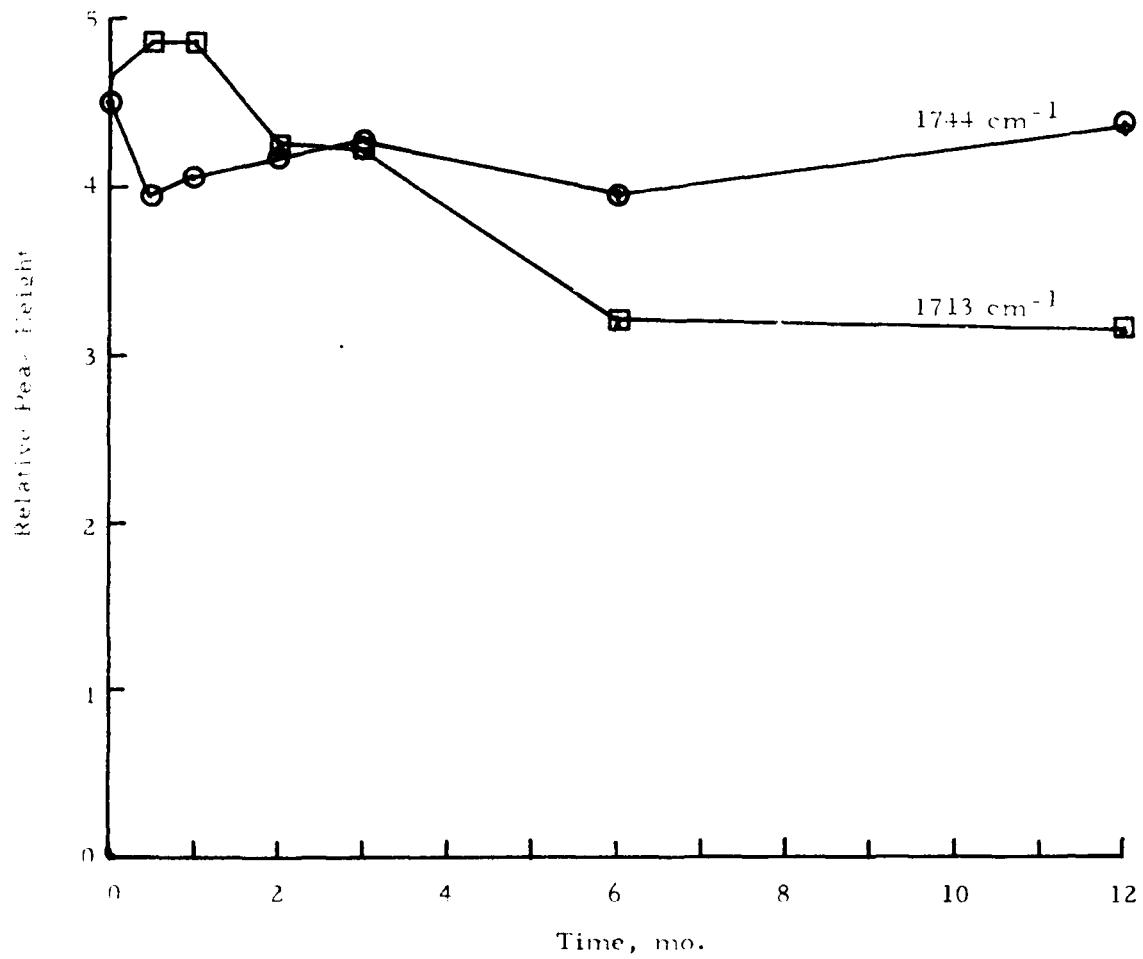
Figure E-13. IR Peak Height Changes With Time.

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TP-H8156/V6-13
Aged at 190°F
Whole Propellant Spectral Data
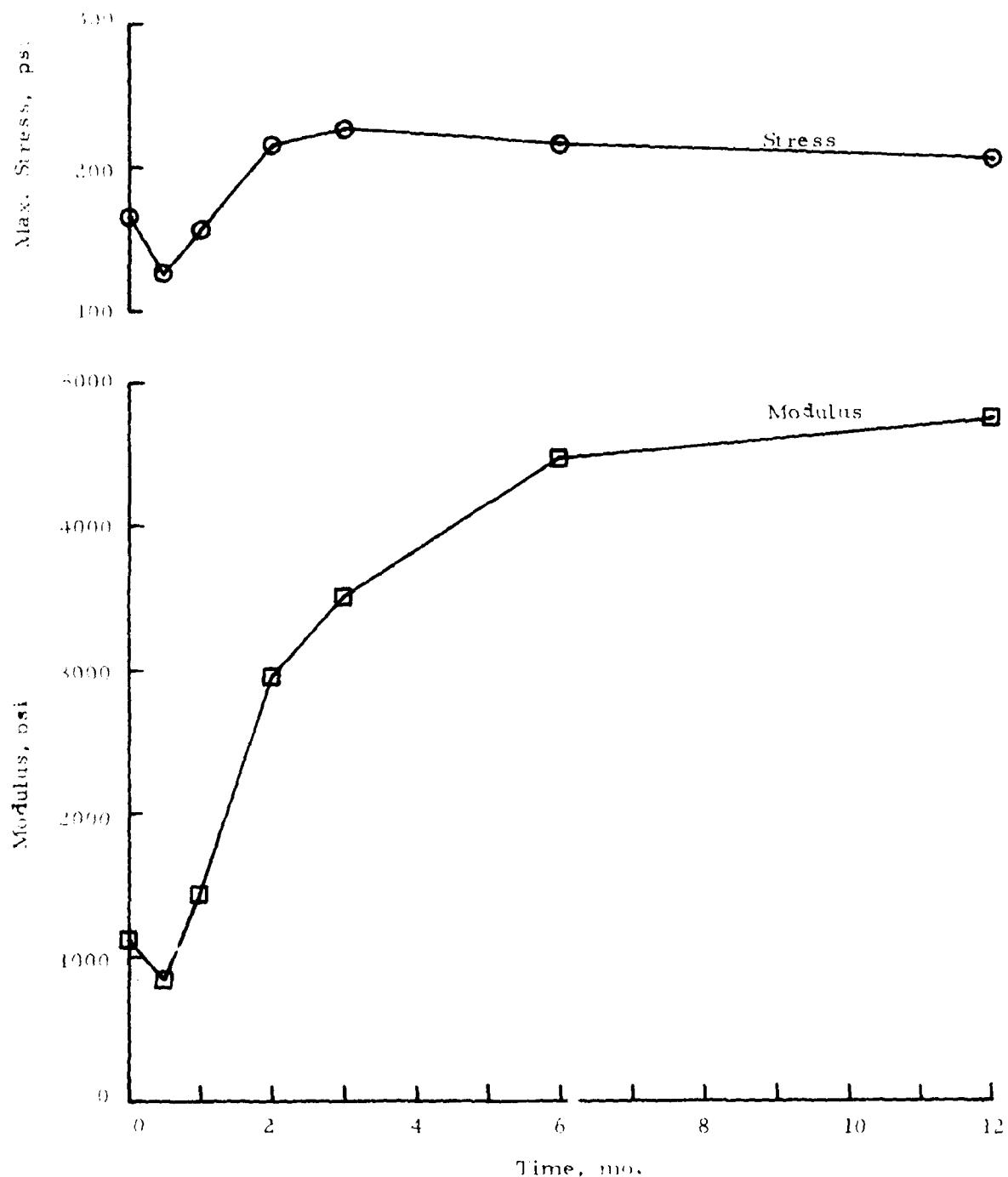
Figure E-14.   Propellant Aging Characteristics

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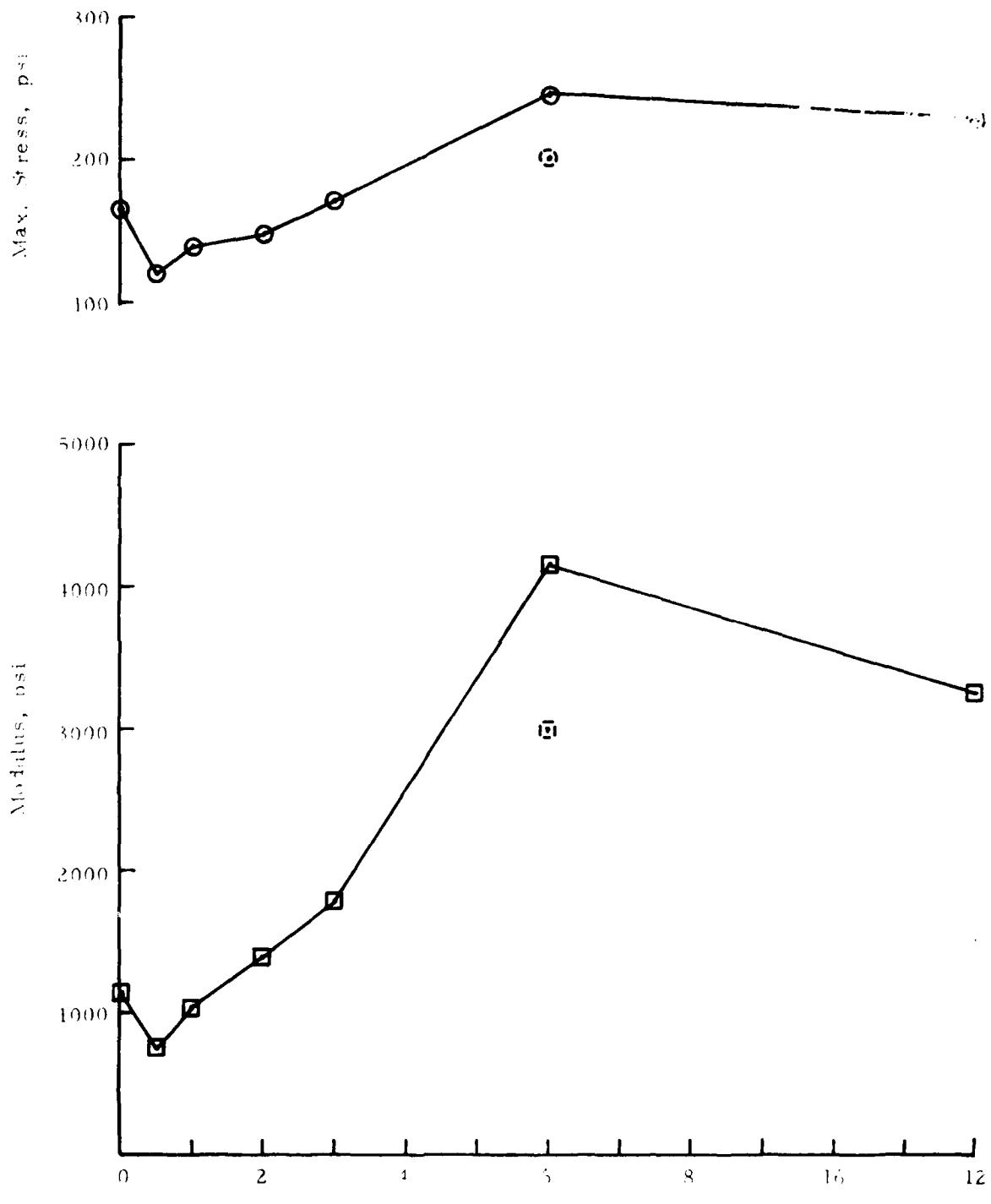
Figure E-15.   Propellant Aging Characteristics

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with modulus and maximum stress were made. Relative peak height plotted against propellant modulus and maximum stress are shown in Figures E-16 and E-17 for the 190° and 170°F correlations.

Correlation of the peak at 1713 cm^{-1} with propellant modulus is a very strong inverse relationship. This is particularly true at the 190°F aging temperature. The correlation is almost equally as strong at the lower aging temperature of 170°F, with the six-month data point falling somewhat off the correlation line. Notice on Figure D-17 that a dotted square has been placed on the graph immediately below the solid square point for six months. If one assumes that the six-months modulus measurement was slightly in error and should have been approximately 3000 rather than near 4150, then the correlation becomes equally strong as that seen with the 190°F aging. Referring now to Figure E-15 and moving the six-months modulus point down to 3000 psi one can see that the modulus curve is smooth and shows a gradual increase in modulus with time.

This inverse relationship of the 1713 cm^{-1} peak height with modulus also carried through to the 150°F aging temperature; however, the correlation was not nearly as strong and there was more scatter in the data. At 130°F this particular correlation apparently disappears; and at 110° and 75°F aging temperature, this correlation with modulus becomes a very strong direct correlation. This change in the direction of the correlation does not imply that the correlation is invalid. It merely indicates that, at 170° and 190°F, the chemical reaction causing this 1713 cm^{-1} peak to change is one that is controlling the mechanical properties of the propellant. At 150° and 130°F this reaction is not nearly so controlling, while at 75° and 110°F there are probably different reactions occurring that tend to make the correlation between the 1713 peak and modulus a direct correlation rather than the inverse correlation found at the very high temperatures (170° and 190°F).

Some very strong correlations were found employing the 1744 cm^{-1} peak. Figures E-16 and E-17 show the relationship of this peak to max. stress for the 190° and 170°F aging temperatures, respectively. Notice on these two plots that the data fall into two distinct groups. On Figure E-16 the 0, 1/2, and one-month age times fall in a straight line, indicating a positive slope (or direct correlation) while the two, three, six and 12-months age time appear displaced above the short time aging data, and form a direct relationship having a line approximately paralleling that of the short time aging data. Exactly the same phenomena is observed at the 170°F aging where the short-time aging lines how include the 0, 1/2, 1, 2, and 3-month aging periods while the higher line includes the 6 and 12-months aging. The same assumption concerning the irregularity of the 6 month mechanical property data for the 170°F aging temperature was made for max. stress
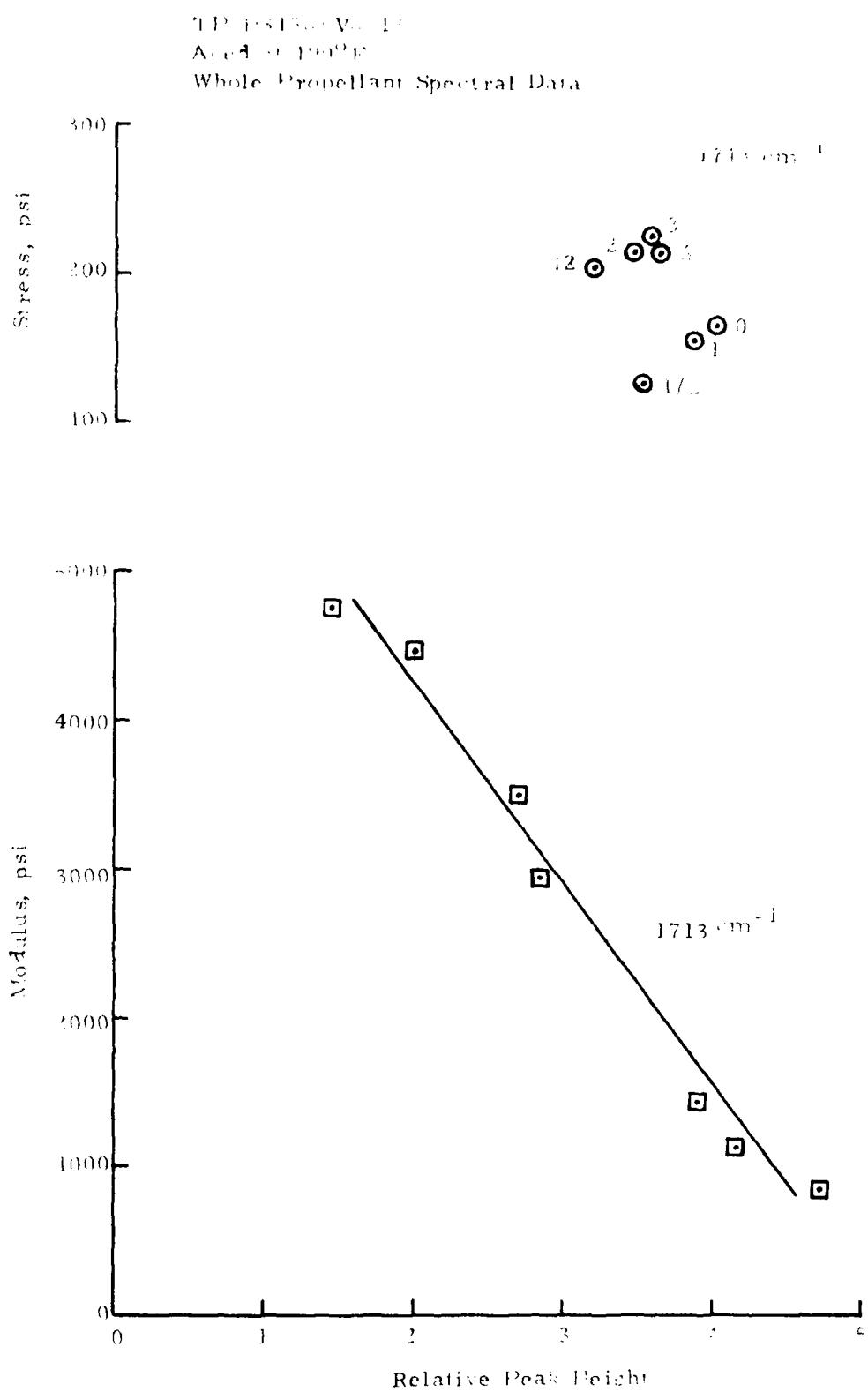
Figure E-16. IR Peak Height Correlations with Mechanical Properties
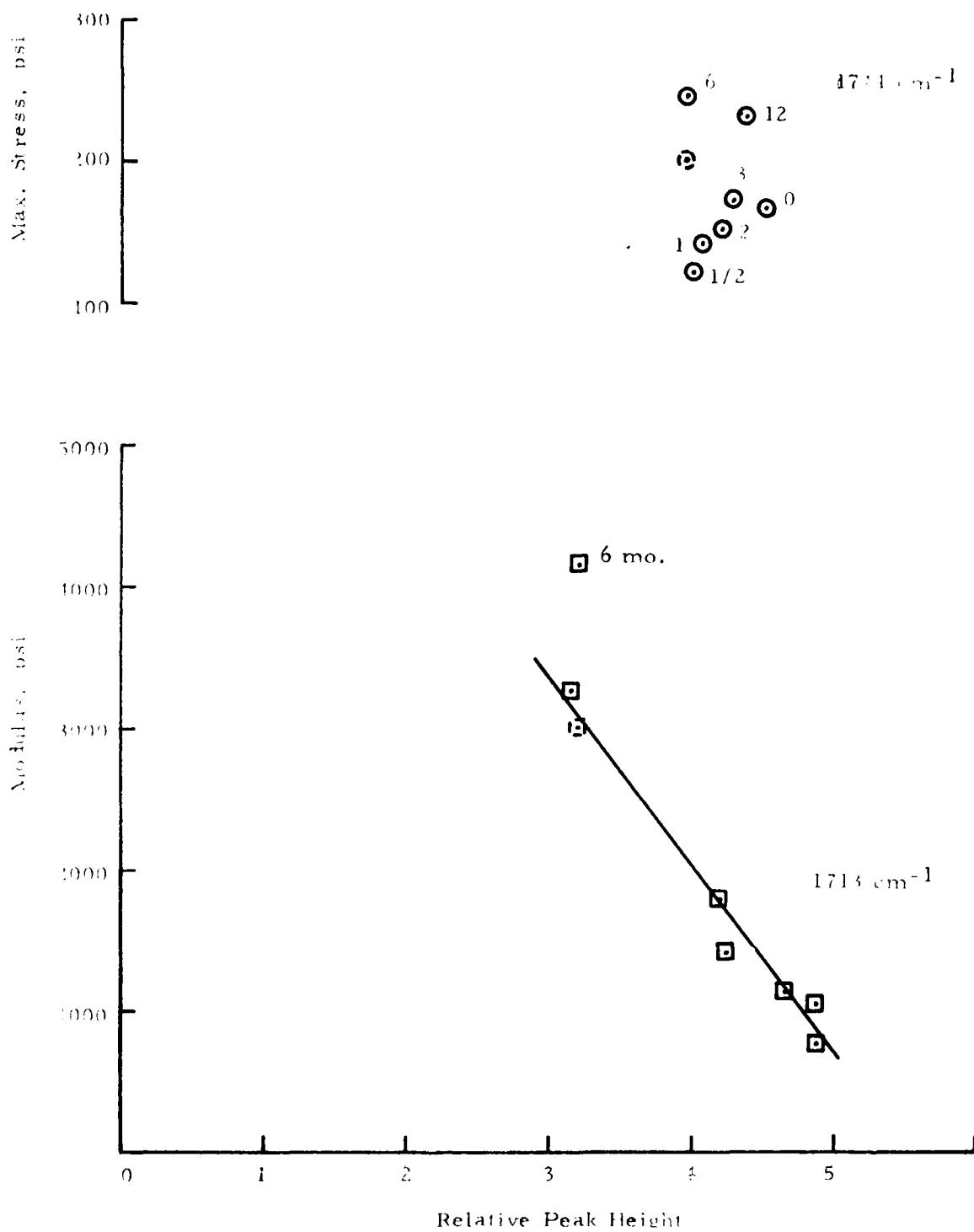
Figure E-17. IR Peak Height Correlations with Mechanical Properties

and looking at the mechanical property curves for the 170°F aging temperature (Figure E-15) one can see that if the stress at 6 months time were 200 psi instead of 245 psi, then the stress-versus-time curve for that propellant would be a much smoother function. Making a similar correction on the Figure E-17 data one sees that the 6-month and 12-month data would form a line that is parallel to the shorter age time line. Our interpretation of this apparent discontinuity in the data at 170° and 190°F is that a second reat which is time and temperature dependent, is induced and causes a sudden increase in the propellant maximum stress that is not totally dependent on the reaction causing the 1744 cm^{-1} peak to change. This same correlation was observed at the other aging temperatures, but the correlation was not as strong as observed at these two high temperatures. At the two median temperatures 130° and 150°F, the correlation seems to disappear and that may indicate another reaction is controlling the degradation at this point. At 110° and 75°F aging, the correlation again becomes very strong and is in the same direction as at the higher temperatures, i.e., it is a direct correlation. Plots of the correlation among the 1713 and 1744 cm^{-1} peaks against modulus and stress are displayed for aging temperatures of 75°, 110°, 130°, and 150°F on Figures E-18 through E-21, respectively.

Correlations at 1713 and 1744 cm^{-1} with Mechanical Properties of Propellant Aged for 12 Months at Various Temperatures

After observing the correlation of these two peaks with modulus and maximum stress (where age temperature was a constant and time a variable) it then became of interest to see if the correlation would hold for propellant aged a constant time at various temperatures. A separate computer data reduction was performed using individual spectra for the conditions where age of the propellant was 12 months and the aging temperature was 75°, 110°, 130°, 150°, 170°, and 190°F. The peak heights and age temperature data are given in Table E-2. A plot of these data is displayed on Figure E-22. A plot of the mechanical properties of the propellant under the same conditions is displayed in Figure E-23. On these two figures, notice the similarity in curve shape for the maximum stress curve and the peak height at 1744 cm^{-1}. There is an equally strong and inverse relationship between modulus and the peak height at 1713 cm^{-1}. A plot of these two spectral peaks against their correlating mechanical properties is given on Figure E-24.

The peak at 1713 cm^{-1} has a very strong inverse relationship to modulus over the temperature range of 130° to 190°F. The very low temperature data points fall off this curve, which is to be expected because of the observed change in direction of this correlation at the 75° and 110°F aging where age temperature was a constant and age time the variable (see Figures E-18 and E-19.).

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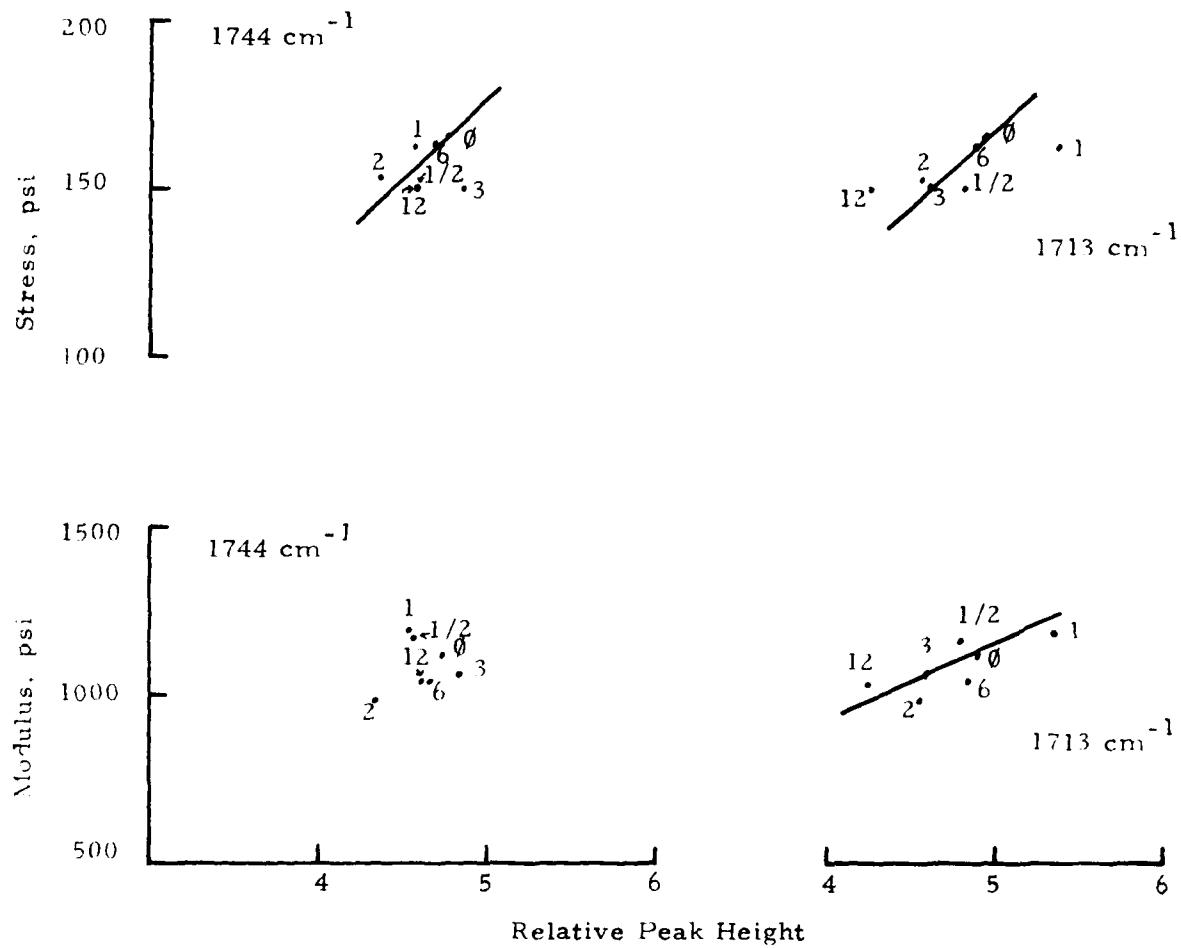
Figure E-18. IR Peak Height Correlations with Mechanical Properties
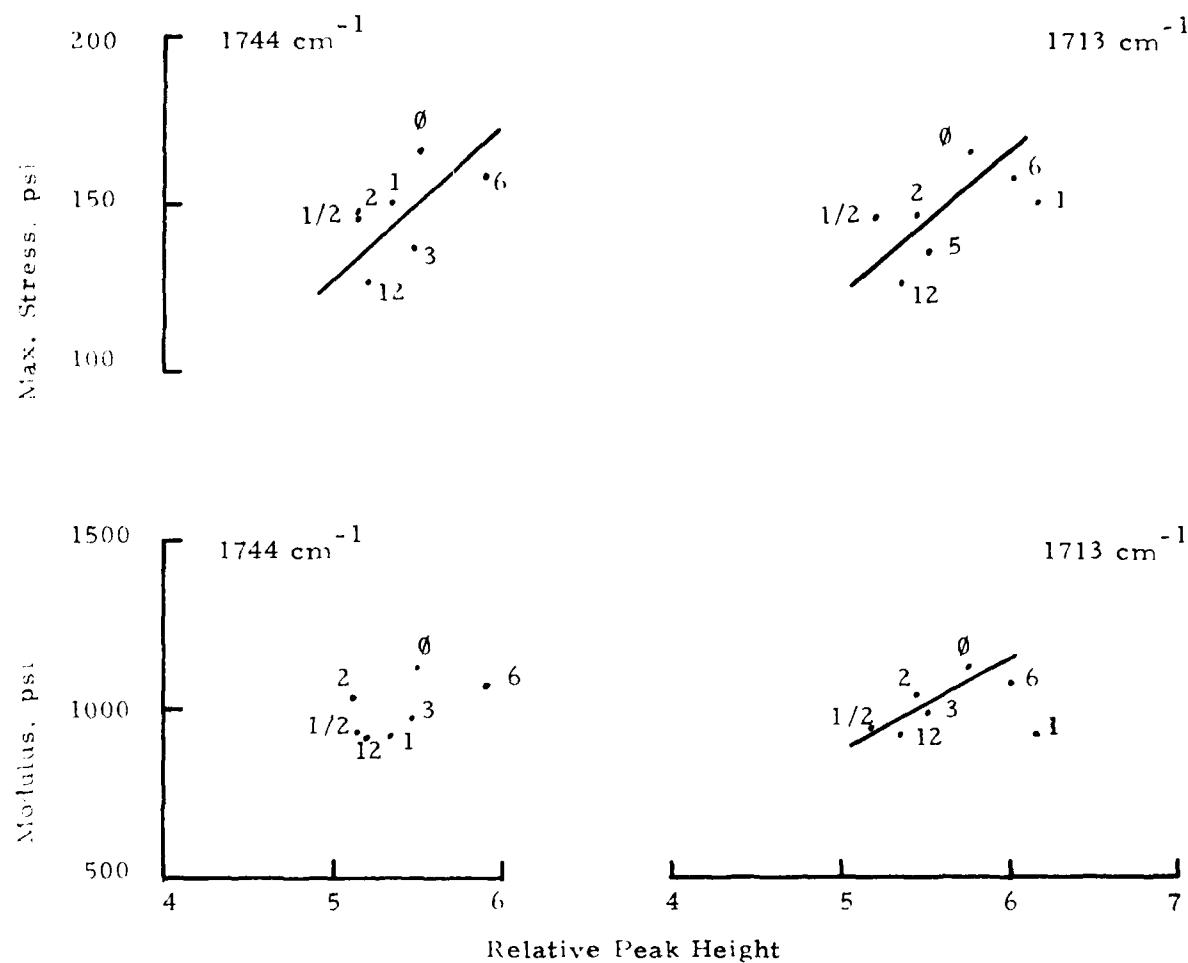
Figure E-19. IR Peak Height Correlations to Mechanical Properties
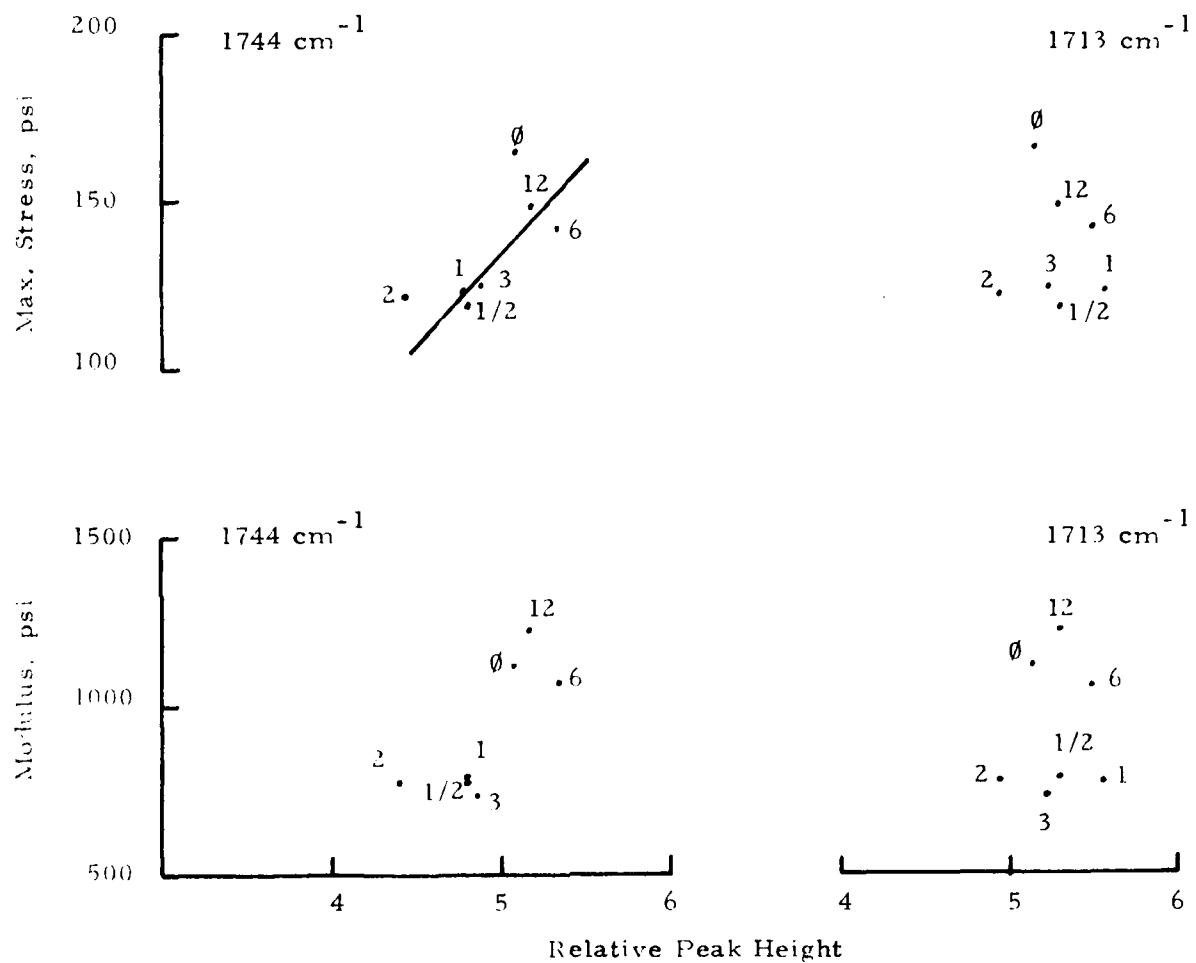
Figure E-20. IR Peak Height Correlations with Mechanical Properties
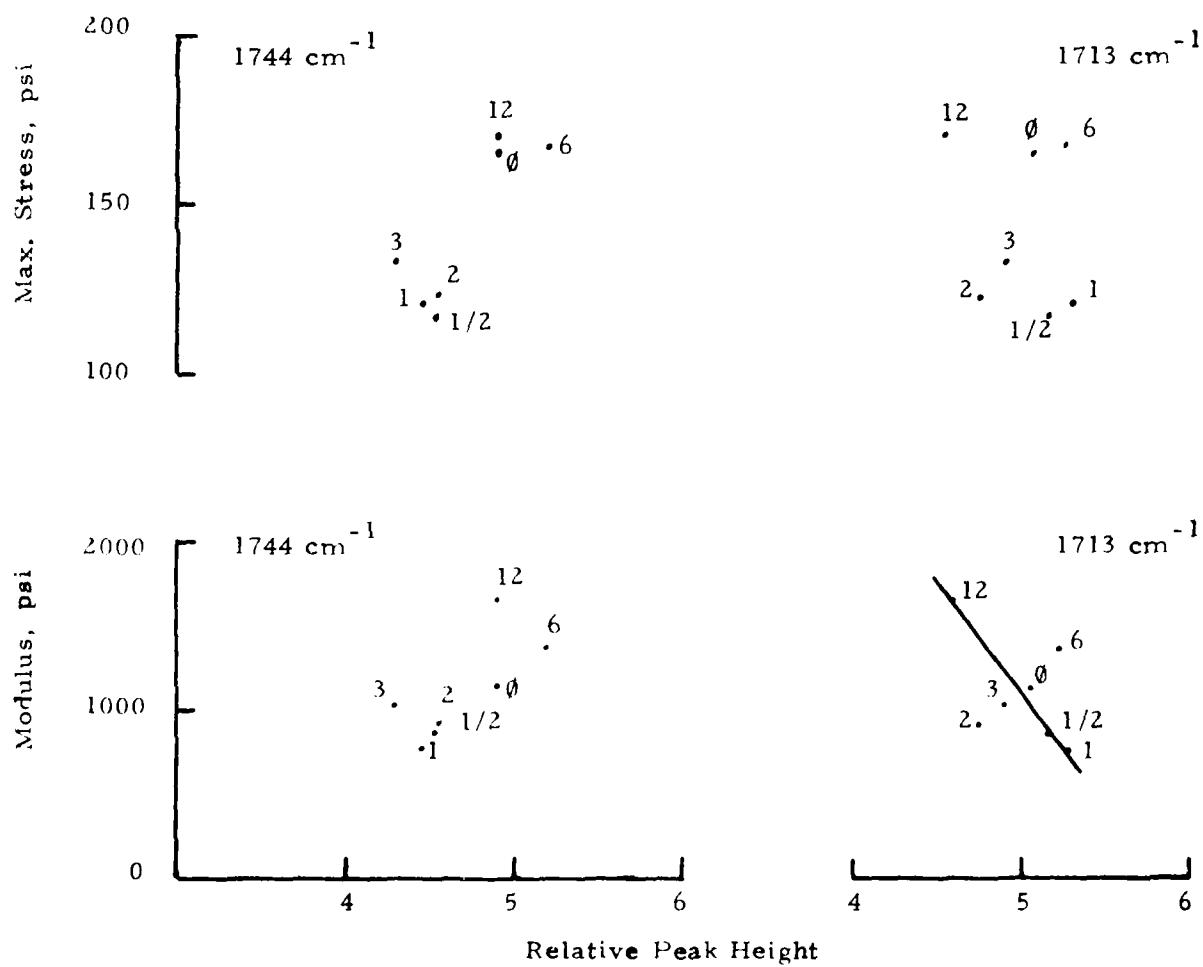
Figure E-21. IR Peak Height Correlations with Mechanical Properties

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TABLE E-2

TP-H8156/V6-13 AGED FOR 12 MONTHS
AT VARIOUS TEMPERATURES

Wave No., cm^{-1}	Age Temperature, $^{\circ}$F					
	75	110	130	150	170	190
1744	3.670	3.577	3.768	3.771	3.698	3.250
1713	3.392	3.649	3.862	3.538	2.696	1.747

NOTES:

(a) Spectra by Barnes ATR/KRS-5.

(b) Data reduced using common baseline for peaks at 1744 and 1713 cm^{-1}.

(c) Spectral information (amplitudes and wave numbers) came from computer normalized data. Normalized at 2920 cm^{-1}.

(d) Whole propellant, spectra taken immediately after tensile testing of propellant.

TP-H8156/ V6-13
Aged 12 months at various temperatures
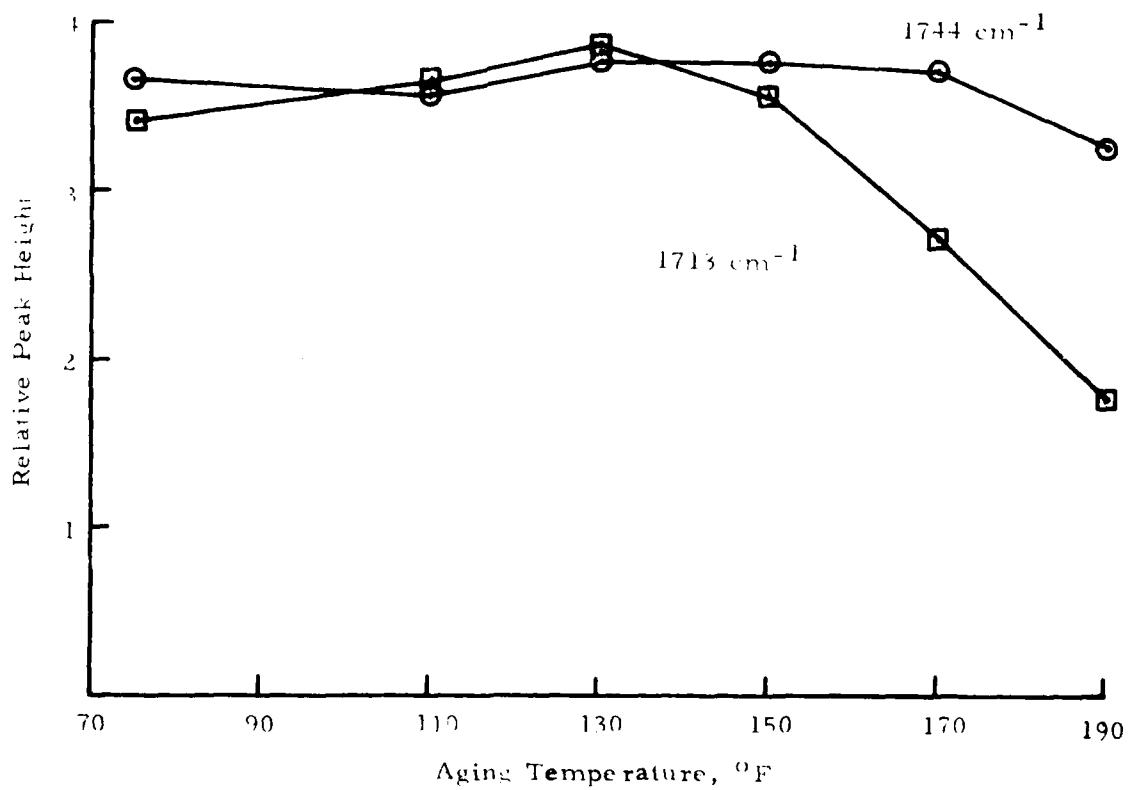
Figure E-22. Relationship of Peak Height (1713 and 1744 cm^{-1}) to Age
Temperature at a Constant Time.

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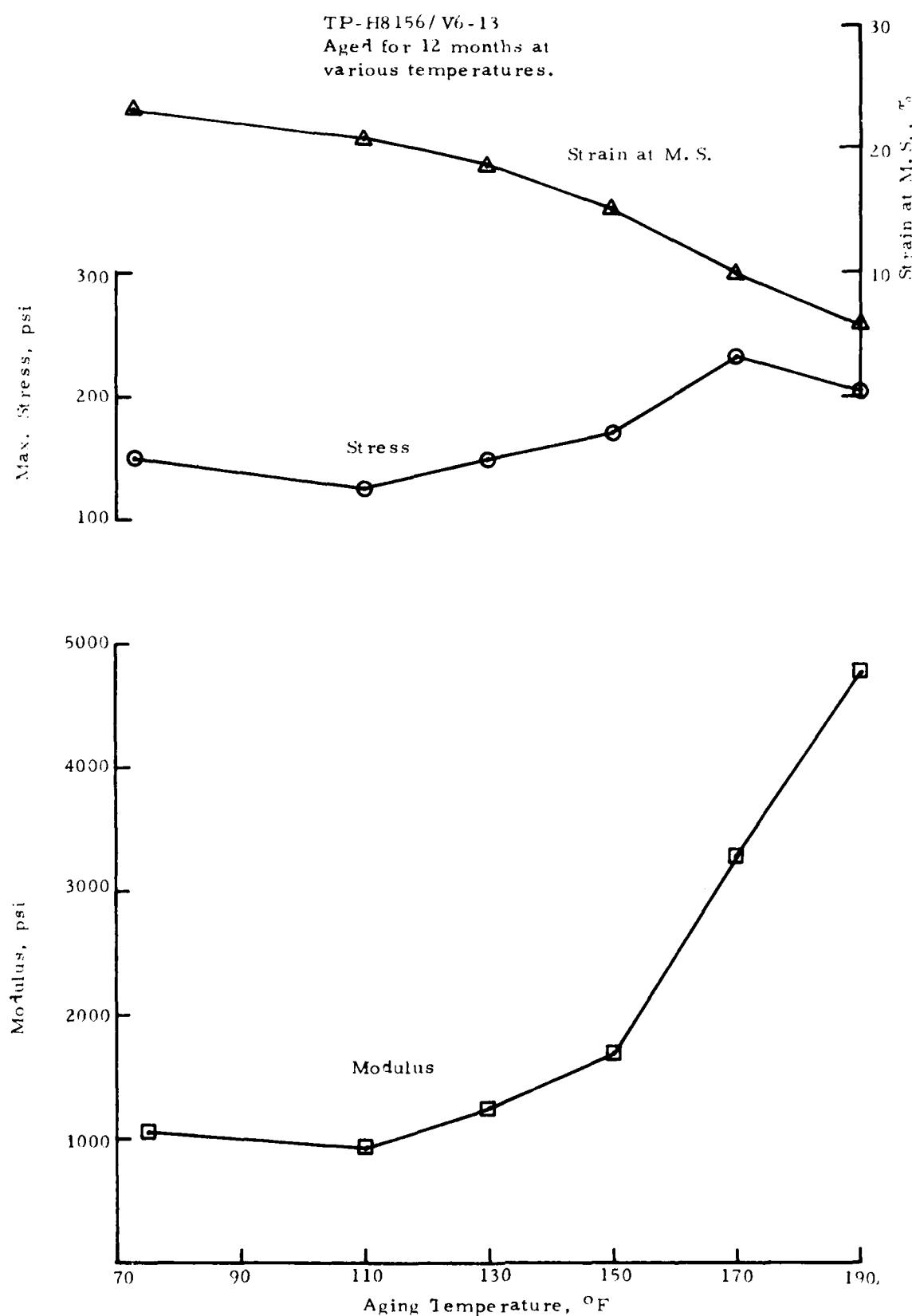
Figure E-23.   Mechanical Properties of TP-H8156 Aged 12 Months at
Various Temperatures

Aged 12 months at various temperatures
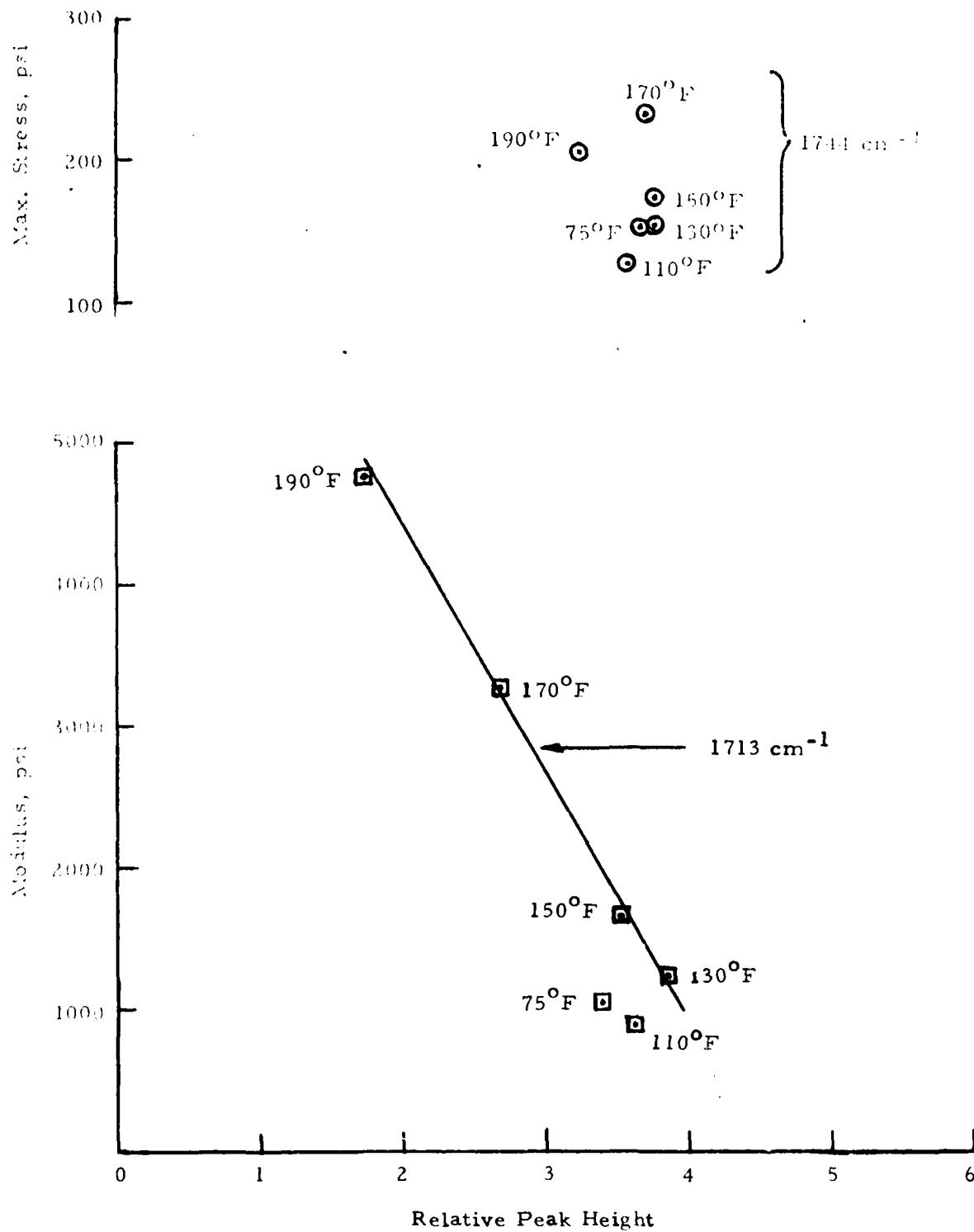
Figure E-24. IR Peak Height Correlations With Mechanical Properties.

Again, a discontinuity in the relationship of the 1744 cm^{-1} peak and maximum stress was observed (this was noted in discussions concerning the constant age temperature at variable time). The two high temperature aging samples, 190° and 170°F, seem to form a group that is above and displaced to a lower relative peak height from the lower temperature aging group of 75° through 150°F. This discontinuity in the relationship is due to the same phenomena described for the 170° and 190°F aging temperature. It could easily be due to two sequential reactions where, for example, reactant A + reactant B -- product C. When the concentration of C has increased to some critical level, C reacts with D to yield E. There is an indication from the correlation that the first reaction proceeds for all conditions, but the second reaction proceeds only where the time and temperature combinations are correct to yield a high enough concentration of C to cause the second of the two reactions to proceed. When the second reaction does occur, it then exerts a strong influence on stress and the reaction that was causing the 1744 cm^{-1} peak to change becomes less noticeable and does not exert near the control over maximum stress that it did at the lower temperature/time conditions.

Other Correlations Found in Propellant Aged 12 Months at Various Temperatures

All peak height changes were examined for the series of spectra representing TP-H8156 propellant aged 12 months at various temperatures. A tabulation of peak heights for this set of propellant samples is given in Table E-3. On this table, the peaks at 1420, 1057, and 941 cm^{-1} are absorptions due to ammonium perchlorate and these would not, therefore, be representative of any change in the organic phase of the propellant. The general amplitude of these three peaks follow each other, a result which is to be expected. It is interesting, however, to note that they also have the same general curve shape as the propellant modulus when plotted against aging temperature. This interesting observation is understandable in light of the way in which the IR spectra are made. One of the standard procedures used in obtaining a propellant spectrum is to adjust the pressure on the plates holding the sample against the ATR prism until a spectrum of a near standard magnitude is obtained. The higher the modulus of the propellant the more pressure must be placed on the plate. The higher the propellant modulus, the less the binder will flow around AP particles and, therefore, leaves an increased number of the AP particle pressed against the ATR prism. Thus, the relative quantity of ammonium perchlorate compared to organic binder apparently increases as the modulus of the propellant increases. The increase in the relative quantity of ammonium perchlorate is merely an indirect measure of the modulus of the propellant. Pressure on the plate is controlled by adjusting the torque on the screws holding the two plates against the ATR prism. This amount of torque is measured, and it was found that the higher the propellant modulus, the greater the torque on the screws to obtain a spectrum of a standard height.

TABLE E-3

TP-H8156 AGED 12 MONTHS, AP UNLEACHED

Peak No.	Wave No, cm^{-1}	Peak Height After 12 Months at Temperature					
		75°	110°	130°	150°	170°	190°
1	3086	1.0425	.9265	.9378	.9962	.8719	.8463
2	3009	.9609	.9601	.9821	1.4066	1.0118	1.1193
3	2993	-	-	-	-	-	.3139
4	2924	16.9563	16.9563	16.9563	16.9563	16.9563	16.9611
5	2855	9.7543	9.6999	9.7222	9.5927	9.6914	9.6231
6	2700	-	-	-	-	-	.1305
7	1744	2.3712	2.3132	2.4651	2.4923	2.6091	2.4174
8	1713	2.0129	2.3557	2.4787	2.2350	1.5905	.9648
9	1697	-	-	-	-	-	.1468
10	1643	1.8372	1.7187	1.7970	1.7436	1.7588	1.7285
11	1613	1.0620	1.0165	1.0266	.9474	.9413	.8561
12	1589	.3265	.3419	.3015	.3023	.3449	.4280
13	1558	-	.1694	.1931	.1793	.1461	.3098
14	1515	4.5789	4.2383	4.1761	3.2467	3.8821	2.2231
15	1420	33.2109	31.9979	30.8983	35.8199	36.0596	56.0189
16	1250	4.2643	3.9264	4.1492	3.8211	3.1567	3.0055
17	1057	23.7163	22.8931	18.7490	24.6866	22.3300	58.8905
18	972	29.0344	31.0271	25.0566	32.2947	27.1742	32.1823
19	941	4.0436	4.1428	3.6167	4.6929	4.3512	7.2319
20	918	13.9344	13.9545	13.3448	14.8344	13.5831	12.8315
21	833	3.7598	3.8030	3.6907	3.5903	3.1474	3.2205
22	787	.3235	.4682	.5446	.4535	.5908	.5830
23	725	1.3111	1.4366	1.3640	1.4708	2.8857	5.8741
	725	5.2978	5.0056	4.5714	5.2111	5.0323	5.8740

Hand calculated using min-to-min connector: 755 → 640 cm^{-1}.

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A typical spectrum from this series is shown on Figure E-25. Note on this spectrum that all non-AP peaks are relatively small and the number of peaks totally uninfluenced by ammonium perchlorate is also quite small compared to a sample of propellant where the ammonium perchlorate has been removed by leaching with water (see Figure E-26).

Those peaks that were large enough to show some change were examined for their correlation to propellant mechanical properties. Other large peaks in the spectrum, even though they were influenced by the presence of ammonium perchlorate were also examined, specifically, those peaks at 972 and 918 cm^{-1}. These latter two peaks show only a very general correlation with propellant modulus and, therefore, were not plotted.

Correlation of peak height changes at 1744 and 1713 cm^{-1} with mechanical properties have just been discussed. A correlation was also found with changes in the height of the peak at 1515 cm^{-1}. This peak correlated reasonably well with strain at max. stress and correlated well with maximum stress. A plot of these correlations is given in Figure E-27. This correlation of the change in the height of the peak at 1515 cm^{-1} has been observed before, and this correlation is indeed the reason why we started examining normalization at 1515 cm^{-1}. We could not envision chemical mechanism by which the peak that is representative of the quantity of curing agent would change with aging time and temperature. This is another example of the fact that this change does apparently take place. The mechanism by which the change occurs still cannot be envisioned; nevertheless, the correlation is there and it is in fact quite strong.

The next peak found to correlate was at 1250 cm^{-1}. It correlated quite well with strain at max. stress and also with maximum stress, but not quite as well. The sign of the two correlations are reversed from each other, as would be expected because of the stress versus strain relationship. These correlations are plotted on Figure E-28.

An examination of the spectra of propellant aged at 75°F for 12 months revealed that there were no peaks which showed a correlation of their change with changes in propellant mechanical properties. This is not too surprising, perhaps, in view of the fact that the propellant itself did not change during storage at 75°F.

Correlations of Propellant Aged at Constant Temperature With Mechanical Properties

An examination of the spectra of propellant aged at 75°F for 12 months revealed that there were no peaks that showed a correlation of their changes with changes in propellant mechanical properties. This is not too surprising, especially in view of the fact that the propellant itself did not change during storage at 75°F.

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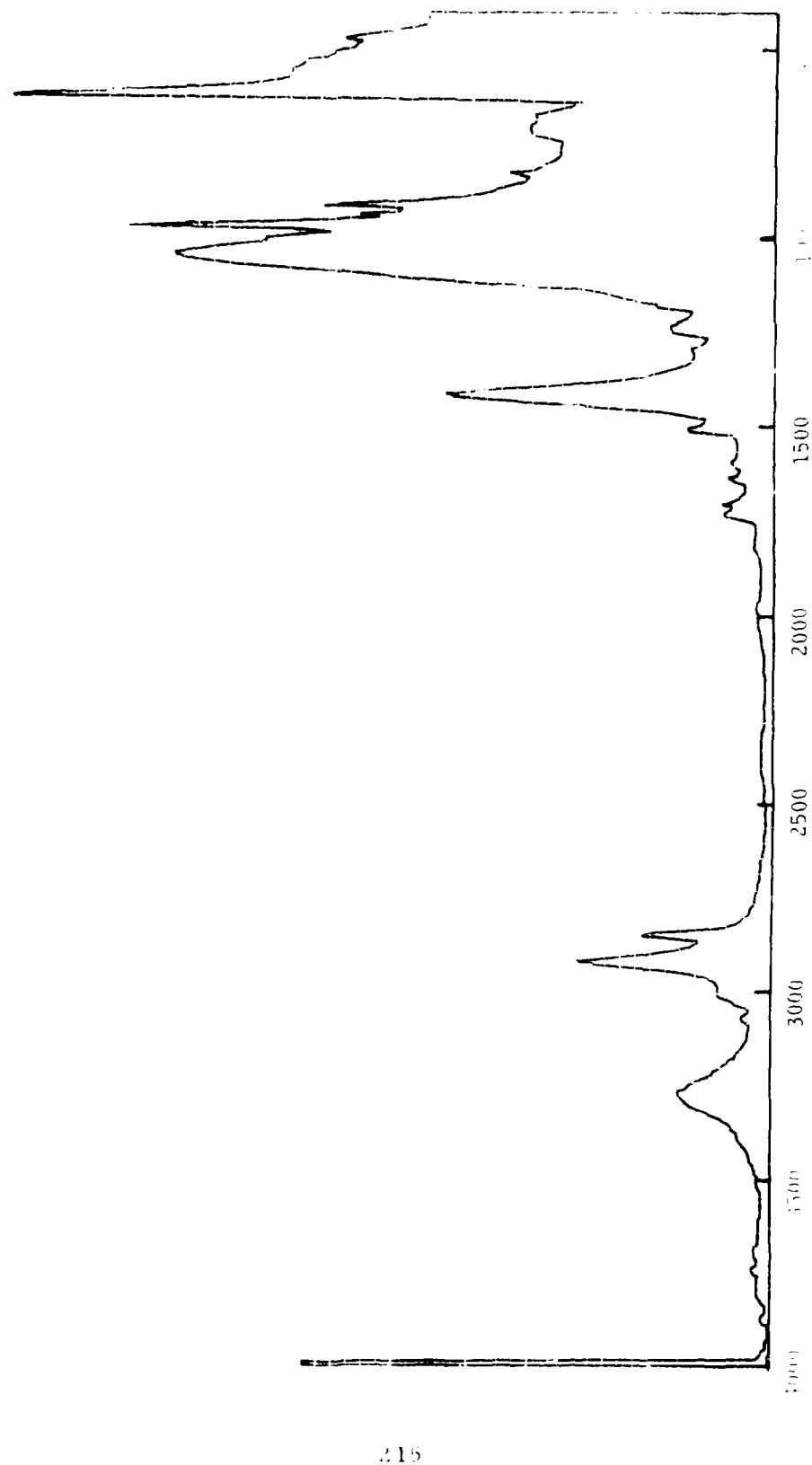
Figure E-25. Typical IR Spectrum of TP-H815, Whole Propellant
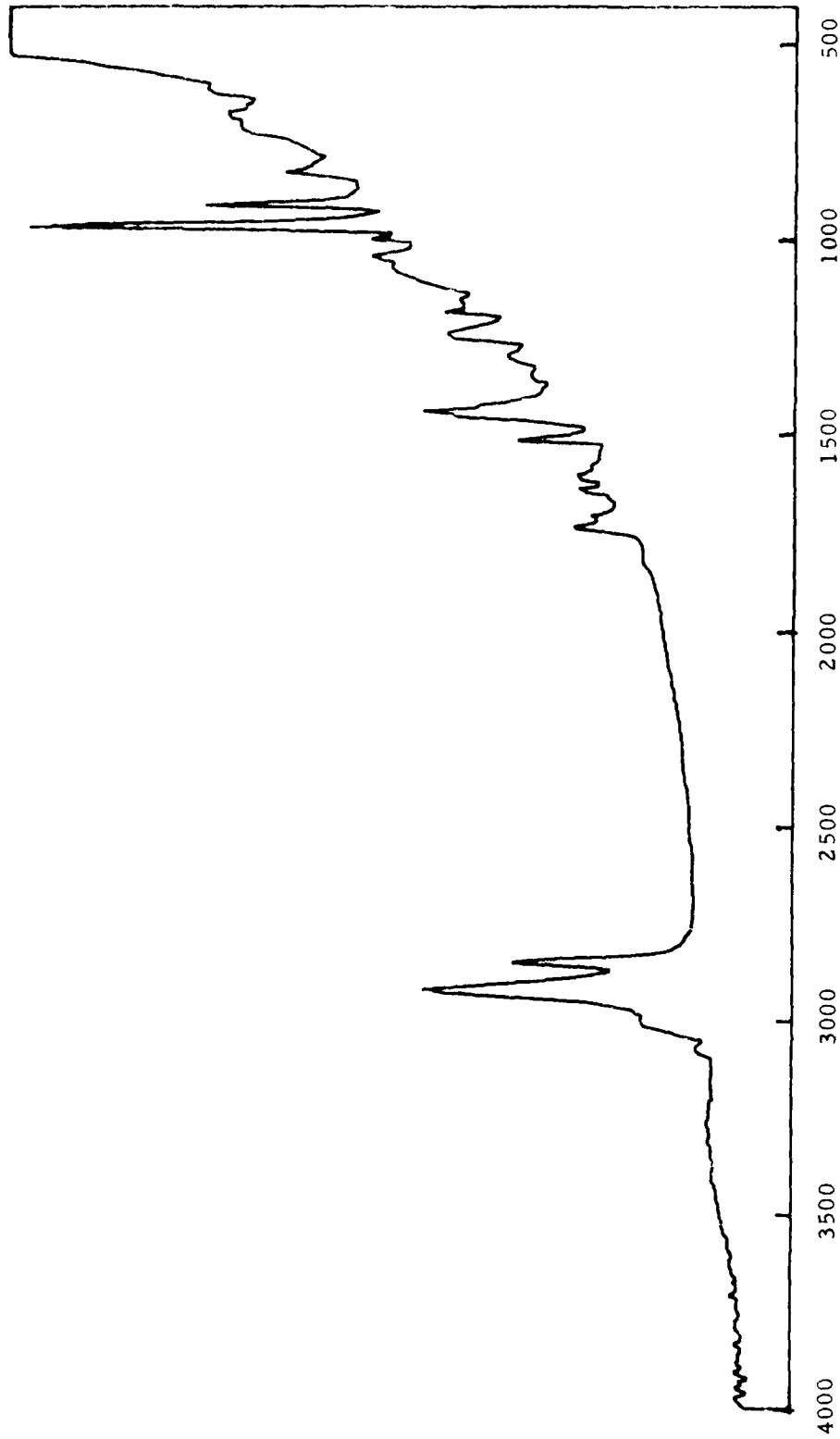
Figure E-26. IR Spectrum of Propellant From Which AP Has Been Leached.
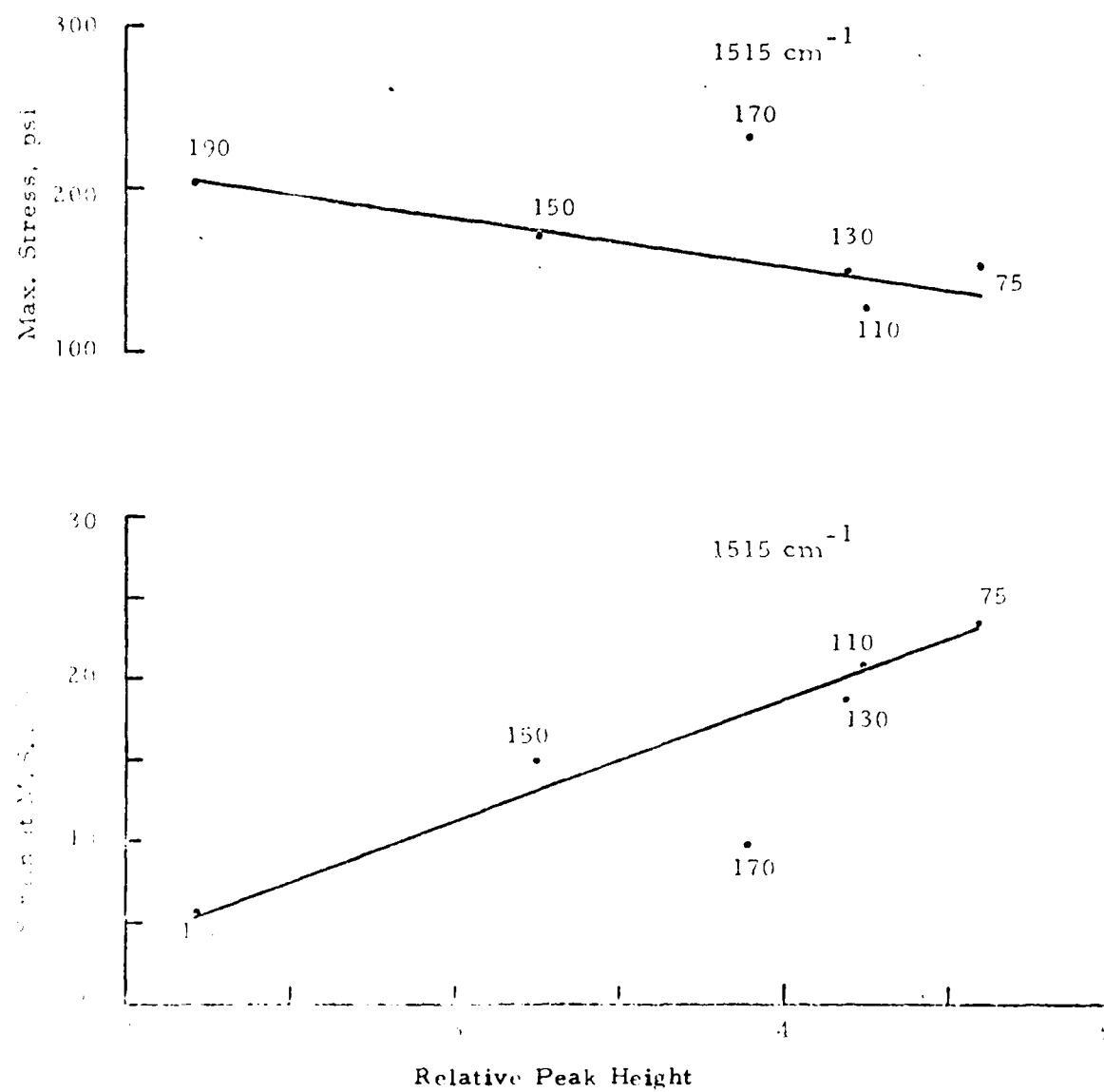
Figure E-27.   Relationship of Spectral Peak Height Changes to
Propellant Mechanical Properties.

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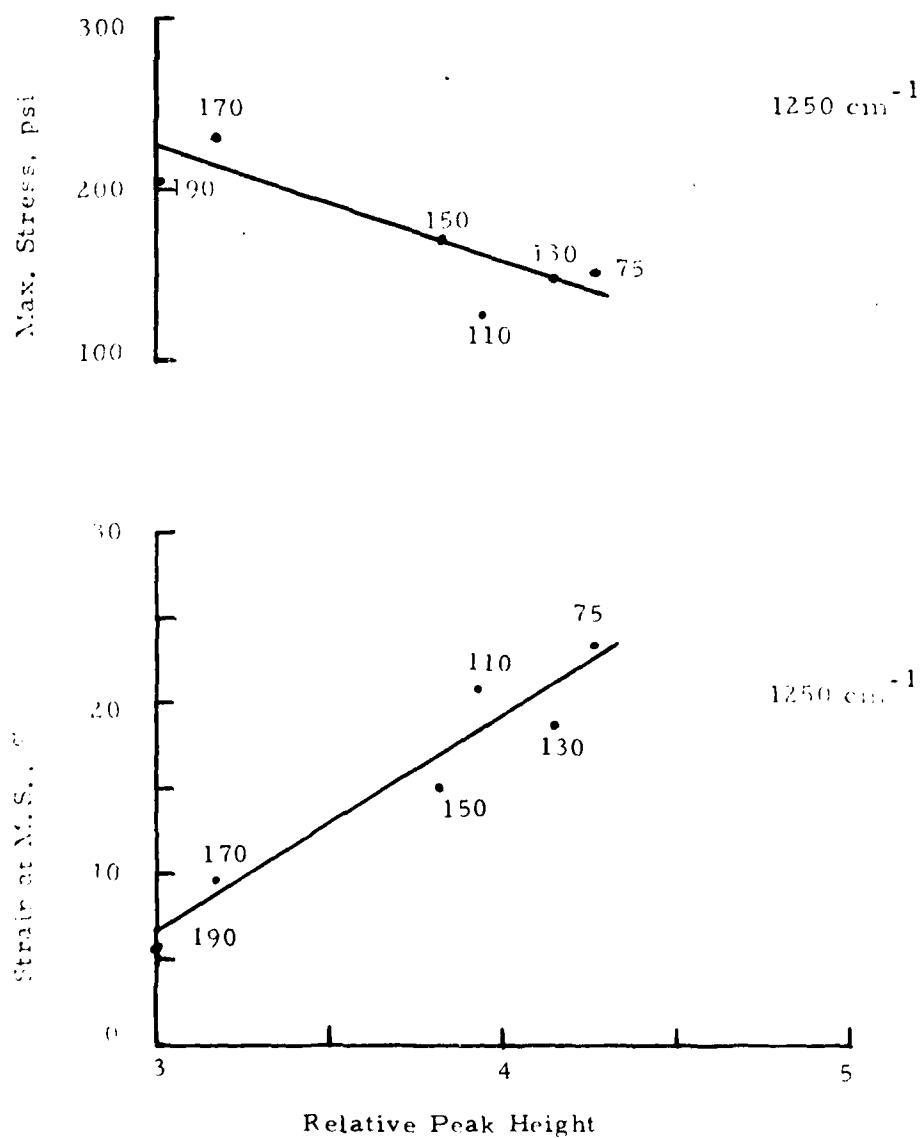
Figure E-28. Relationship of Spectral Peak Height Changes to
Propellant Mechanical Properties.

In examining the spectra of propellant aged at 110°F, we found no additional spectral peaks that could be correlated with changes in propellant mechanical properties. It appeared that the peaks at 918 cm^{-1} and 972 cm^{-1} may have a correlation to the changes in propellant maximum stress. Bearing in mind the previous discussion concerning the response of these peaks to assembly torque, the correlation may not be real, but the data were placed on a plot and the plot is shown in Figure E-29.

An examination of the spectral data for whole propellant aged at 130°F revealed that perhaps the peak at 1250 cm^{-1} might correlate with modulus and strain at maximum stress. Correlation with strain is considerably stronger than the correlation with modulus, but neither of the correlations are exceptionally strong (Figure E-30). The propellant itself did not change very much and its variation in strain at maximum stress over the one year time period was very slight, so one would not expect to find any really large changes in the infrared spectrum of the aged propellant.

Infrared spectra propellant aged at 150°F provided one fairly strong correlation, that being peak height change at 1250 cm^{-1} (Figure E-31) with changes in strain at maximum stress. This is the correlation that "almost developed" in the 130°F aged propellant. Mechanical properties of the propellant aged at 150°F are beginning to show fairly substantial changes over the one-year time period. Therefore, one would expect to begin to see some changes in the organic spectrum of the aged propellant.

Propellant aged at 170°F underwent some very distinct changes in mechanical properties over the one-year period, and examining the spectra of whole propellant, we found a very distinct correlation between the peak at 1250 cm^{-1} and strain at maximum stress. A correlation that was equally as good was found with that same mechanical property and the peak located at 1520 cm^{-1}. These correlations are shown on Figure E-32.

Propellant aged at 190°F for 12 months underwent some rather large changes in its mechanical properties. A very strong correlation was found between the changes in the peak height at 1250 cm^{-1} and 1520 cm^{-1} with strain at maximum stress. These correlations are plotted on Figure E-33.

Thus, it seems that, when the propellant mechanical properties change considerably, there are several peaks in the propellant spectrum which change correspondingly. Figures E-27 and E-28 show again the responses of the peaks at 1520 cm^{-1} and 1250 cm^{-1} to changes in propellant mechanical property where age time is a constant and age temperature is one of the variables. Thus, for this particular propellant, TP-H8156, we have found four peaks in the infrared spectrum of whole propellant which correlate linearly with changes in propellant mechanical properties. These spectral peaks being at 1744, 1713, 1250, and 1520 cm^{-1}. One or more of these spectral peaks can be correlated with one or more of each of the three propellant mechanical properties - stress, strain, and modulus. Thus, it appears to be entirely possible to take the infrared spectrum of whole propellant and establish a firm linear correlation between the IR spectrum and the mechanical properties of the propellant.

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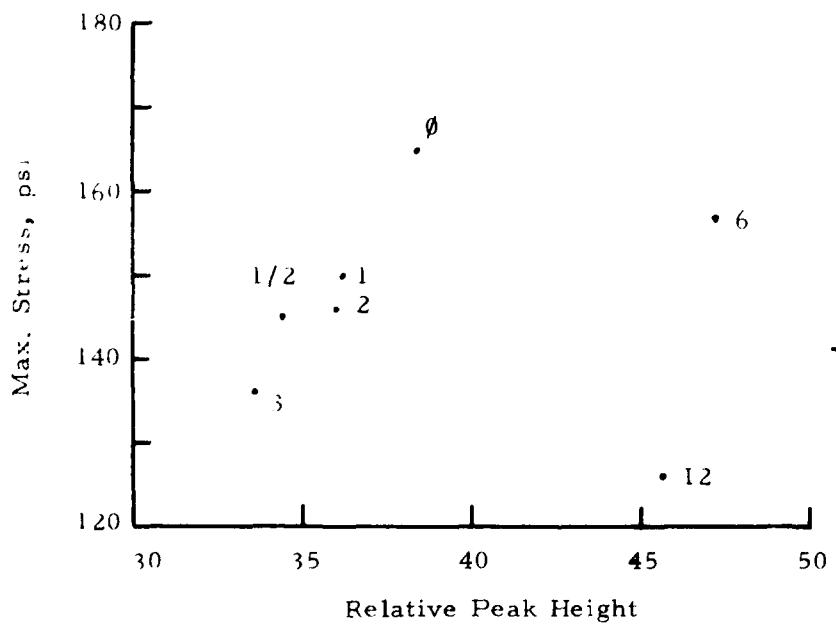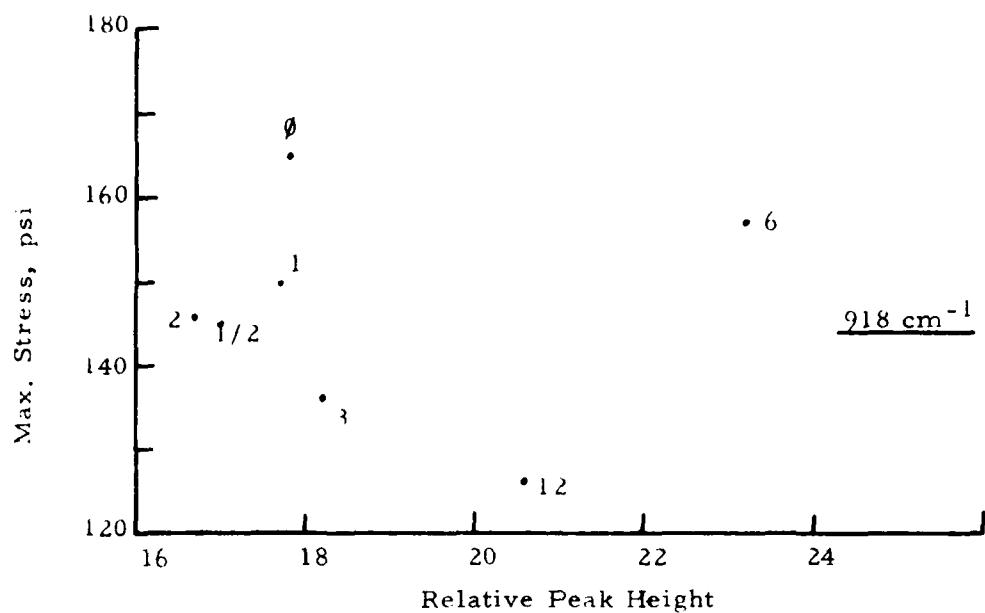
Figure E-29. Correlation of Peaks at 972 cm^{-1} and 918 cm^{-1}, and Stress.

TP-H8156/V6-13 Aged 12 mo. at 130°F

Whole propellant spectral data
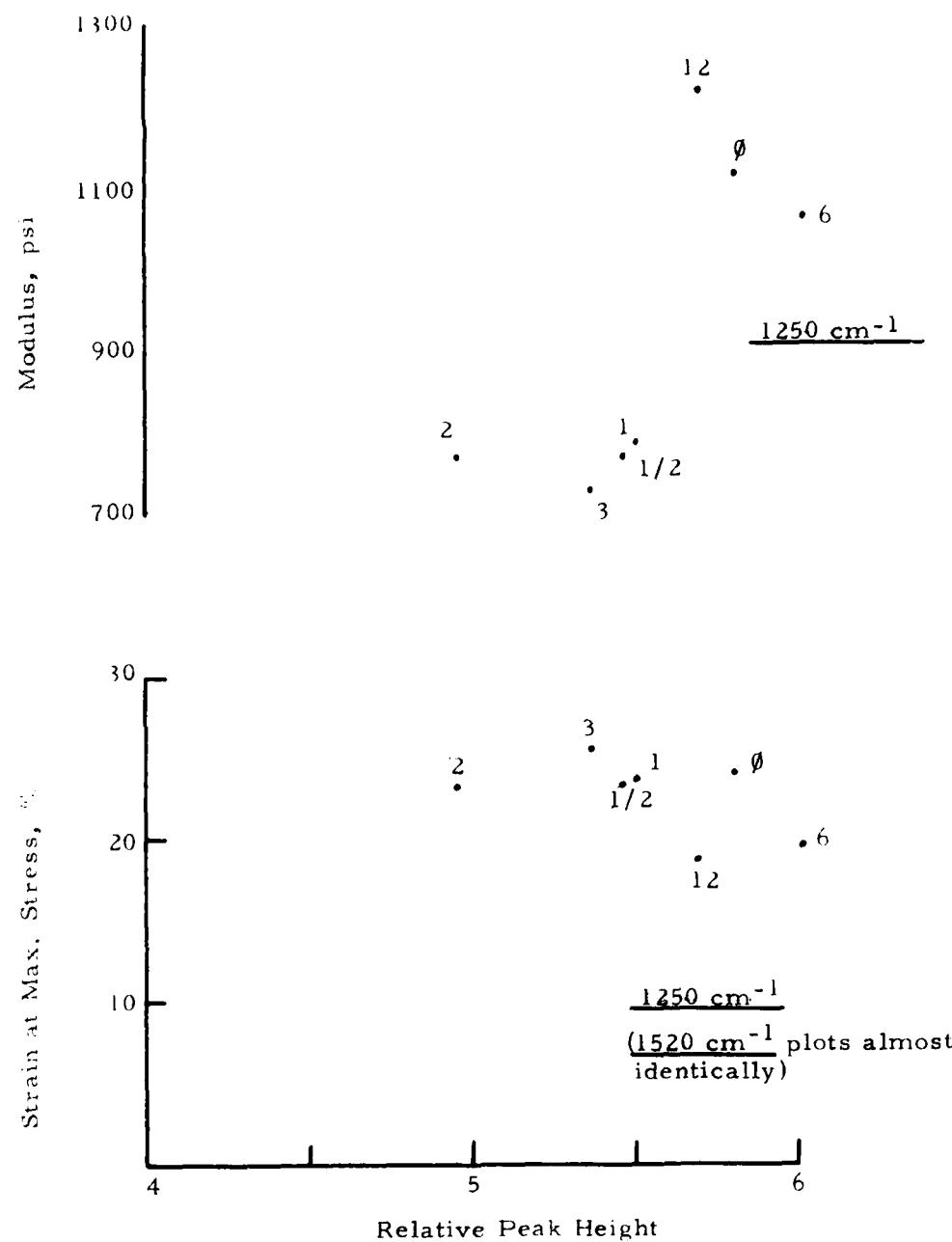
Figure E-30. Correlation of Peak at 1250 cm^{-1}, Modulus and Strain.

TP-H8156/V6-13 aged 12 mo. at 150°F

Whole propellant spectral data
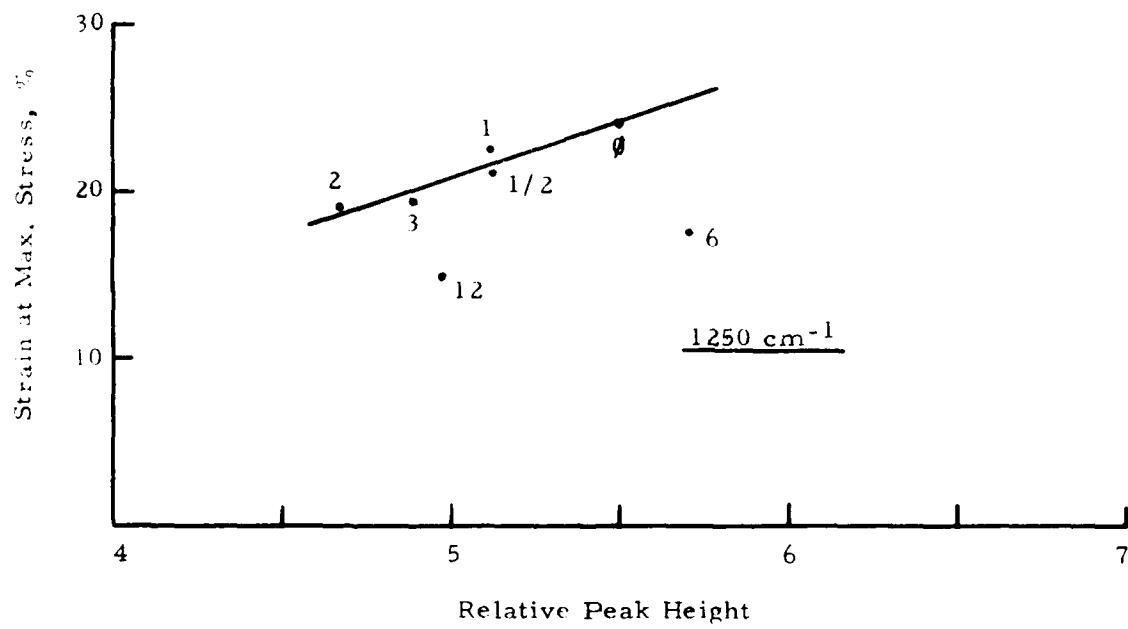
Figure E-31. Correlation of Peak at 1240 cm^{-1} and Strain.

TP-H8156/V6-13 Aged 12 mo. at 170°F

Whole propellant spectral data.
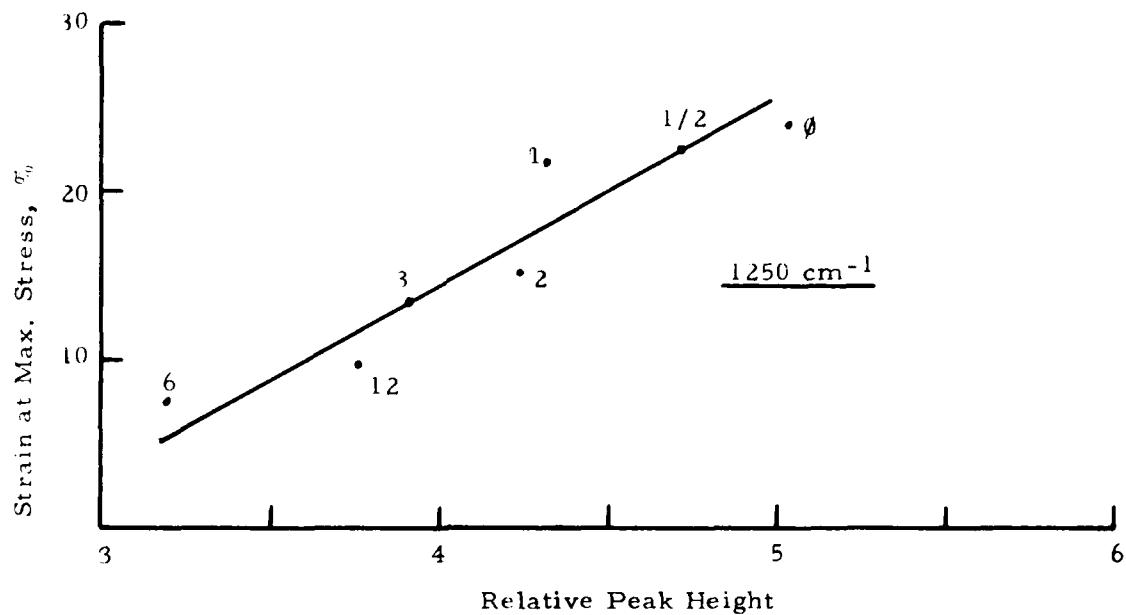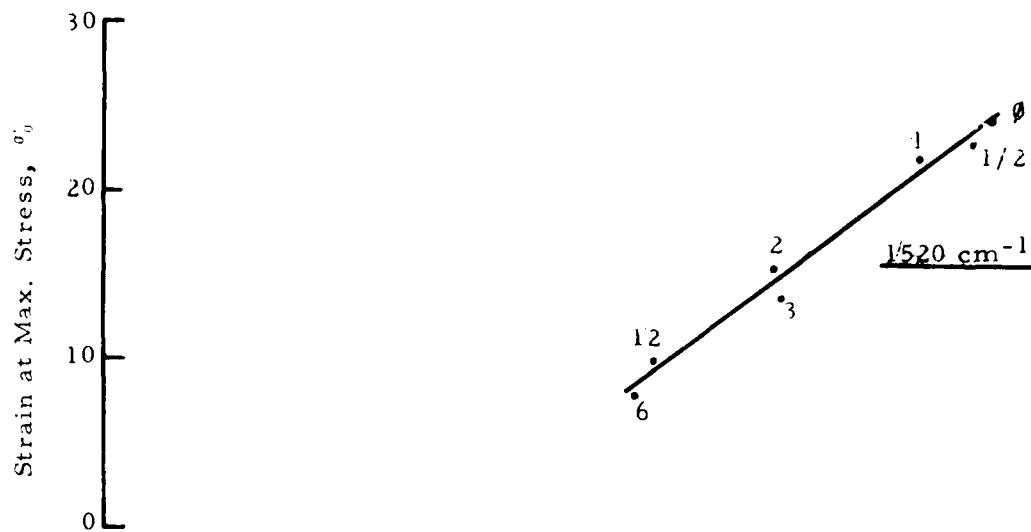
Figure E-32. Correlation of Peaks at 1250 cm^{-1} and 1520 cm^{-1} and Strain.
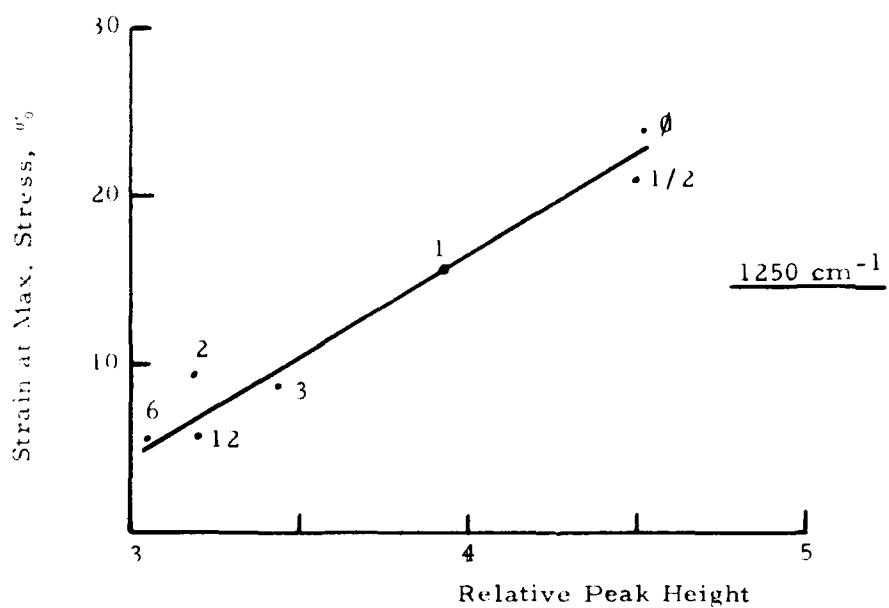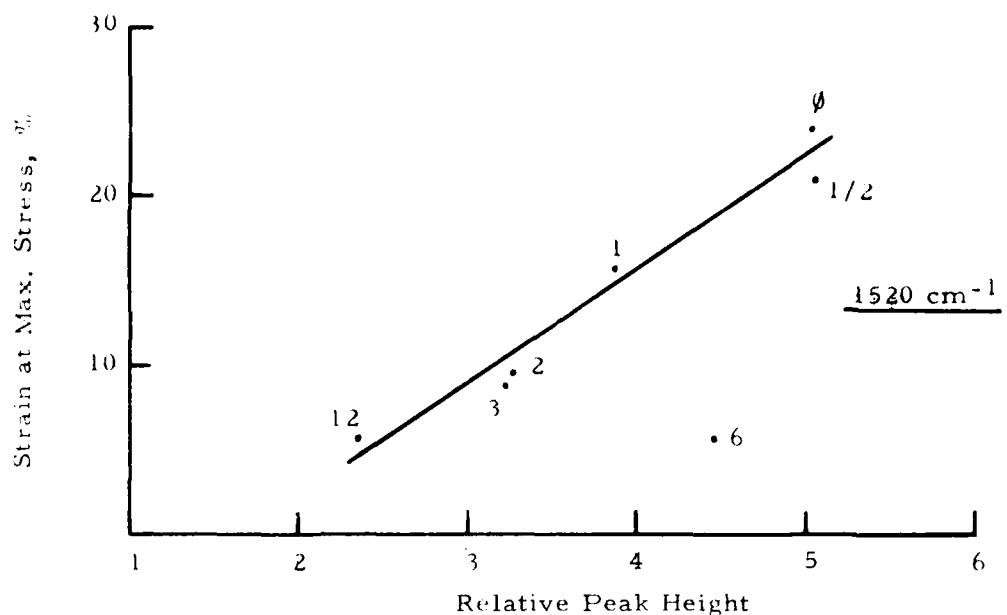
Figure E-33. Correlation of Peaks at 1250 cm^{-1} and 1520 cm^{-1}, and Strain

Using the plots shown on Figures E-24, E-27, and E-28, we can take the infrared spectrum of a sample of this propellant, reduce the data by computer methods, and tell exactly what the mechanical properties of that piece of propellant are. Information presented on Figures E-31, E-32, and E-33 merely serve to reinforce the data plots.

CONCLUSIONS CONCERNING AP LEACHING AND DATA CORRELATIONS

1) Leaching ammonium perchlorate from propellant removes some organic material from the propellant in addition to removing the ammonium perchlorate. Although this makes the organic portion of the propellant spectrum more visible, it does change the nature of the correlations that are found between peak height changes and mechanical property changes.

2) Propellant from which ammonium perchlorate has been leached does have valid correlations between peak height changes and propellant mechanical properties.

3) Leaching ammonium perchlorate from propellant adds a step in the analysis of the propellant which may not be necessary. Certainly, for the propellant that we examined in this series, that step would not be necessary. For other propellant formulations, it may be a very necessary step.

4) Valid correlations are found with whole propellant in spite of the spectral influence of ammonium perchlorate. In fact, more correlations were identified with whole propellant than with propellant from which ammonium perchlorate had been leached.

5) Correlating spectral changes where time is a constant and aging temperature is the variable provides more valid correlations than does the case where age temperature is a constant and aging time is the variable. In the former case, the mechanical properties of a propellant can be identified from a plot of spectral peak height changes versus mechanical property where time is the constant and age temperature is the variable.

6) The case described in conclusion 5 will permit us to take a piece of propellant, regardless of how it has been aged and determine its mechanical properties merely by analyzing its infrared spectrum. This would be particularly important in determining the mechanical properties of a rocket motor aged in the field where aging conditions are unknown.

APPENDIX F

CORRELATION OF IR PEAK HEIGHT CHANGES

AND PROPELLANT MECHANICAL PROPERTY CHANGES

FOR TP-H8266 PROPELLANT

The aging plan for TP-H8266 involved aging at four temperatures, 77°, 100°, 145°, and $165^{\circ}F$, with test points at 0, 2, 4, 8, 16, 24, 36, and 52 weeks; thus, there were available a total of 29 IR spectra for the correlation of IR data with propellant mechanical properties.

Analysis of the IR spectra was commenced when the propellant had been aged through 36 weeks; and, to start with, the propellant aged at 165° F was treated. The seven data points for the $165^{\circ}F$ were analyzed using the IR data reduction program E-490; and these spectral data, along with the mechanical properties, were input to the statistical data analysis program.

A large number of simple correlations were found for modulus, stress, and strain at maximum stress with certain of the infrared peaks. Three multiple correlations were also found ... one each for modulus, strain at maximum stress, and stress. All of these correlations are listed in Table F-1. Note that for the simple correlations, all values have a confidence level of 95% with one value being close to a 99% confidence level. In the multiple correlations, the modulus equation has a confidence level very close to 99%, while for the strain at maximum stress and the stress correlations the confidence levels are at the 99% level. The multiple correlations are plotted on Figures F-1, F-2, and F-3, these being for modulus, strain at maximum stress, and stress, respectively. Note on the plot for strain at maximum stress (Figure F-2) that the measured stress values for the propellant do not follow a progressive pattern; i.e., strain increasing or decreasing uniformly with time, but the values appear almost randomly oriented along the measured strain axis. It is very encouraging to note that the IR spectral data follow so that the strain calculated using the equation matches the measured strain very closely at all time periods.

When the 52-week test period was reached, the test data were added to the 36-week data, and a new set of statistical analyses performed. Reduction of IR data for the 52-week time period was identical to that used for the 0 to 36 weeks data reduction. The results of the statistical analysis of the entire set of data for the $165^{\circ}F$ aging is given in Table F-2. A review of those data and comparison of them with the data presented on Table F-1 shows that the peak at 3009 cm^{-1} in both cases correlated with modulus and stress, and the addition of the 52nd week data strengthened the correlation coefficient. The peak at

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TABLE F-1

CORRELATIONS FOR TP-H8266/L-1895
AGED 0-36 WEEKS AT 165°F

Simple Correlations	Coefficient
Peak Height at 3009 cm^{-1} with Modulus	-0.7329
Peak Height at 3009 cm^{-1} with Stress	-0.7724
Peak Height at 2924 cm^{-1} with Strain at MS	0.7410
Peak Height at 1651 cm^{-1} with Stress	-0.7955
Peak Height at 1319 cm^{-1} with Modulus	-0.8436
Peak Height at 1319 cm^{-1} with Stress	-0.8506
Peak Height at 1242 cm^{-1} with Modulus	-0.7020
Peak Height at 972 cm^{-1} with Strain at MS	0.7396

$$r_{.99} = 0.874$$
$$r_{.95} = 0.754$$
$$r_{.90} = 0.669$$

Multiple Correlations

Modulus = 5711 - 835.1(V_2) - 2244(V_7)
  V_2 = Peak Height at 3009 cm^{-1}
  V_7 = Peak Height at 1319 cm^{-1}

$$R = 0.9316$$
$$R^2 = 0.8679$$
$$R_{.99} = 0.949$$
$$R_{.95} = 0.881$$

Ultimate Strain - None

Strain at M.S. = -108.2 + 6.979(V_4) + 1.976(V_6) - 22.45(V_7)
  V_4 = Peak Height at 2924 cm^{-1}
  V_6 = Peak Height at 1651 cm^{-1}
  V_7 = Peak Height at 1319 cm^{-1}

$$R = 0.9953$$
$$R^2 = 0.9906$$
$$R_{.99} = 0.983$$

Stress = -805.2 + 125.1(V_5) - 316.1(V_7)
  V_5 = Peak Height at 2885 cm^{-1}
  V_7 = Peak Height at 1319 cm^{-1}

$$R = 0.9743$$
$$R^2 = 0.9493$$
$$R_{.99} = 0.949$$

TP-H8266/L-1895 Aged 0 through 36 Weeks at 165°F

Whole Propellant Spectra

$$R = 0.9816$$
$$R_{.99} = 0.949$$
$$R_{.95} \quad 0.887$$
$$R^2 \quad 0.8679$$
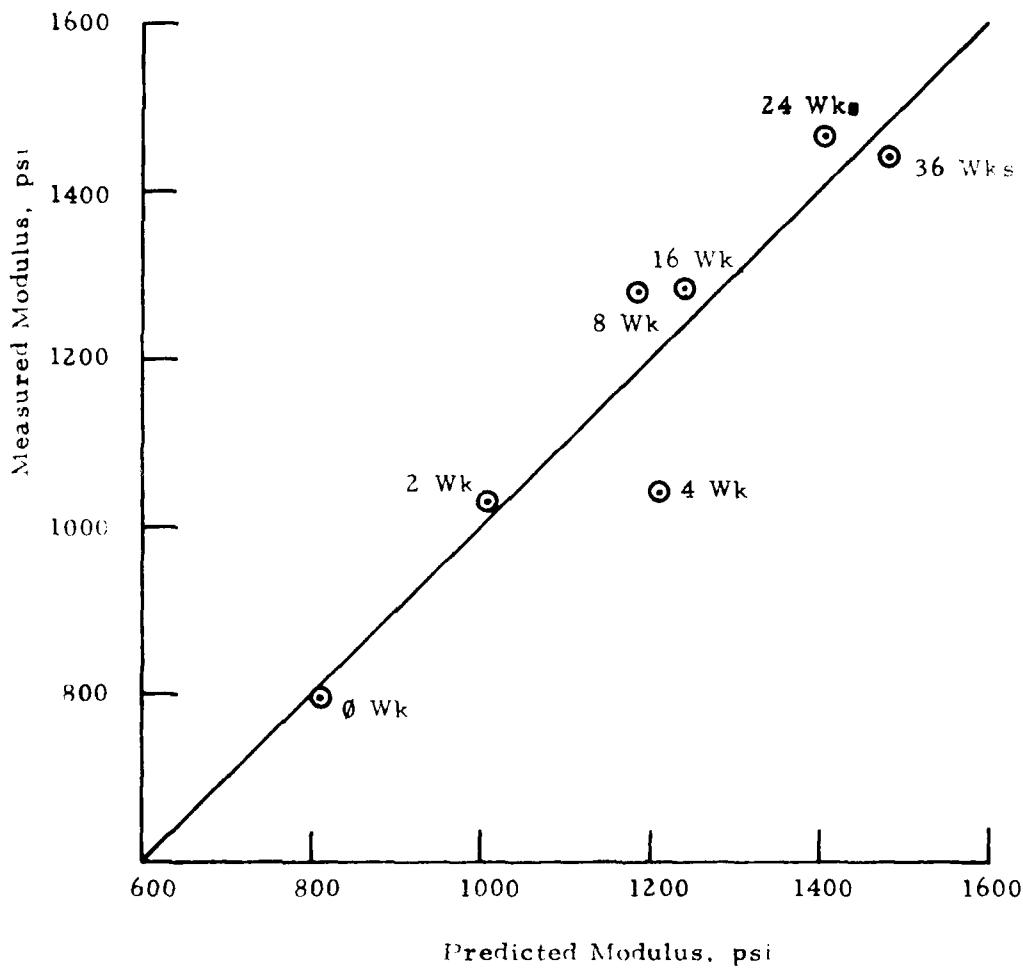
Figure F-1. Multiple Correlation for Modulus

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TP-H8266/L-1895 Aged 0 through 36 Weeks at 165°F

Whole Propellant Spectra

R = 0.9953

R .99   0.9983

R² 0.9906
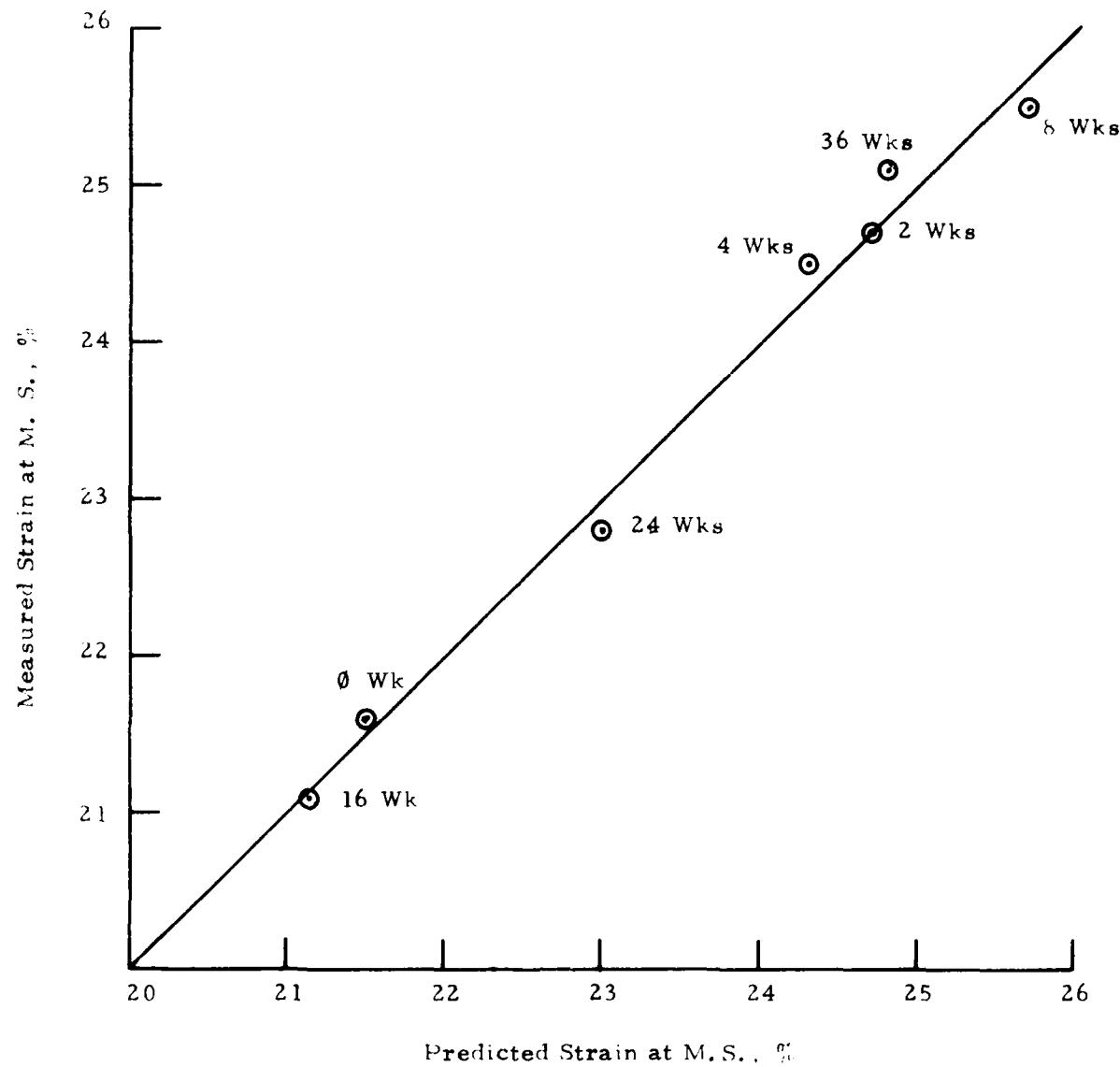
Figure F-2. Multiple Correlation for Strain at Max. Stress

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TP-H8266/1.-1895 Aged 0 through 36 Weeks at 165°F

Whole Propellant Spectra

R = 0.9743

$R_{.99} = 0.949$

$R^2 = 0.9493$
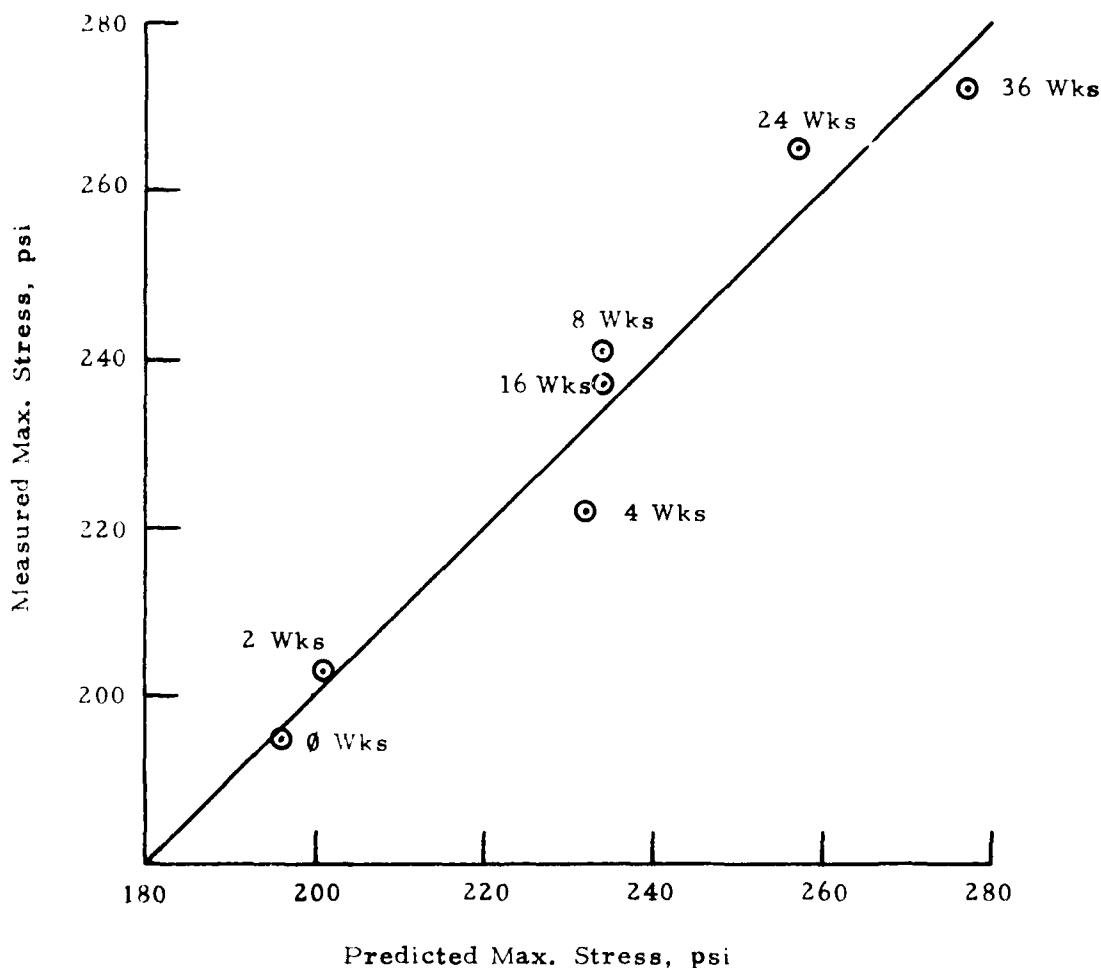
Figure F-3. Multiple Correlation for Max. Stress

TABLE F-2

CORRELATIONS FOR TP-H8266/L-1895

AGED 0-52 WEEKS AT 165°F

(Modified IR Data Reduction)

Simple Correlations	Coefficient
Peak Height at 3009 cm^{-1} with Modulus	-0.8246
Peak Height at 3009 cm^{-1} with Stress	-0.8231
Peak Height at 2885 cm^{-1} with Stress	0.7076
Peak Height at 1651 cm^{-1} with Stress	-0.7495
Peak Height at 972 cm^{-1} with Strain at MS	0.7798

$$r_{.99} = 0.834$$
$$r_{.95} = 0.707$$

Multiple Correlations

Modulus = $7216 - 1300(V_2) - 1680(V_7)$ $R = 0.9194$
     V_2 = Peak Height at 3009 cm^{-1} $R^2 = 0.8452$
     V_7 = Peak Height at 1319 cm^{-1} $R_{.99} = 0.917$

Ultimate Strain = $-24.97 + 1.461(V_9) + 10.66(V_{11})$ $R = 0.8347$
     V_9 = Peak Height at 972 cm^{-1} $R^2 = 0.6967$
     V_{11} = Peak Height at 779 cm^{-1} $R_{.99} = 0.917$

Strain at M.S. = $-2.838 + 1.074(V_9)$ $R = 0.7798$
     V_9 = Peak Height at 972 cm^{-1} $R^2 = 0.6081$
                               $R_{.99} = 0.834$
                               $R_{.95} = 0.707$

Max. Stress = $880.0 - 128.3(V_2) - 41.93(V_6) - 117.8(V_7)$ $R = 0.9829$
     V_2 = Peak Height at 3009 cm^{-1} $R^2 = 0.9661$
     V_6 = Peak Height at 1651 cm^{-1} $R_{.99} = 0.962$
     V_7 = Peak Height at 1319 cm^{-1} $R_{.95} = 0.912$

1651 cm^{-1} correlated well with stress, but the addition of the 52nd-week data decreased the correlation coefficient somewhat, but it still left it at the 95% confidence level. The peak at 972 cm^{-1} correlated again with strain at maximum stress, and a definite strengthening of the correlation coefficient took place when the 52nd-week data were added. Some of the correlations found for the first 36 weeks of testing were dropped out when the 52nd-week data were added. Simple correlation coefficients on Table F-2 for 0 to 52 weeks of aging are at least at the 95% confidence level.

Among the multiple correlations that were found when the 0 to 52-week data were analyzed was that there were correlations for modulus, strain at maximum stress, ultimate strain, and maximum stress. These correlations are shown also in Table F-2. The modulus equation on Table F-2 shows the same two peaks (3009 and 1319 cm^{-1}) as was found for the 0 to 36-week data (Table F-1). The magnitudes of the coefficients for these two variables changed somewhat, but the magnitude of the correlation coefficient decreased only very slightly and is still at the 99% confidence level. The equation for ultimate strain in Table F-2 is new to this data set; because, at the earlier time (0 to 36 weeks), there was no multiple correlation for ultimate strain.

The correlation for strain at maximum stress has been strengthened somewhat simply because it is now dependent only upon the peak height at 972 cm^{-1}, while at the 36-weeks test point, there were three peak heights involved in determining the value for strain at maximum stress. Where aging was for 0 to 52 weeks, this strain at maximum stress equation was statistically significant at the 95% level.

Data shown on Table F-2 for the multiple correlations are plotted on Figures F-4, F-5, F-6, and F-7 for modulus, ultimate strain, strain at max. stress, and stress, respectively.

After having treated the propellant aged at 165°F, we then took the entire group of spectra (29 spectra) and ran them through the IR data reduction computer program as a unit.

In reducing these 29 IR spectra an unintentional change was made in the spectrum that was used as the "NPHOTO" for the common baseline routine. In the common baseline routine the computer uses a spectrum which the user designates as the best "picture" of the appearance of a region of the spectra for which a common baseline is drawn. In order to reduce IR data for a propellant containing DOA as the plasticizer, the 2850 cm^{-1} peak must be used for normalizing. To obtain a valid measure of the height of that peak, it must be measured from a baseline between 3100 to 2750 wave numbers. In establishing the height of the normalizing peak the computer always searches for the peak within a specified wave number range and measures from the specified

TP-118266/L 1895
Aged 0 - 52 Weeks at 165°F
Whole Propellant Spectra

R = 0.9194
R^2 = 0.8452
$R_{.99}$ = 0.8823
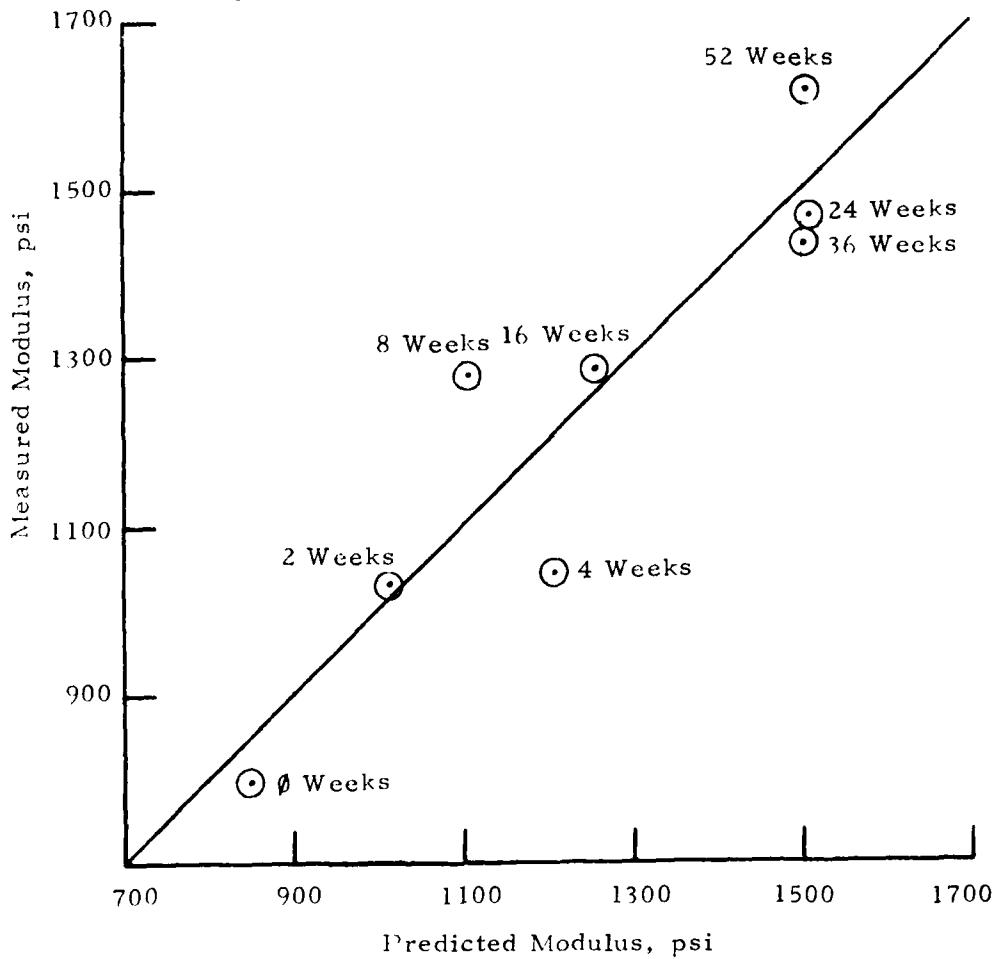
Figure F-4.Multiple Correlation for Modulus

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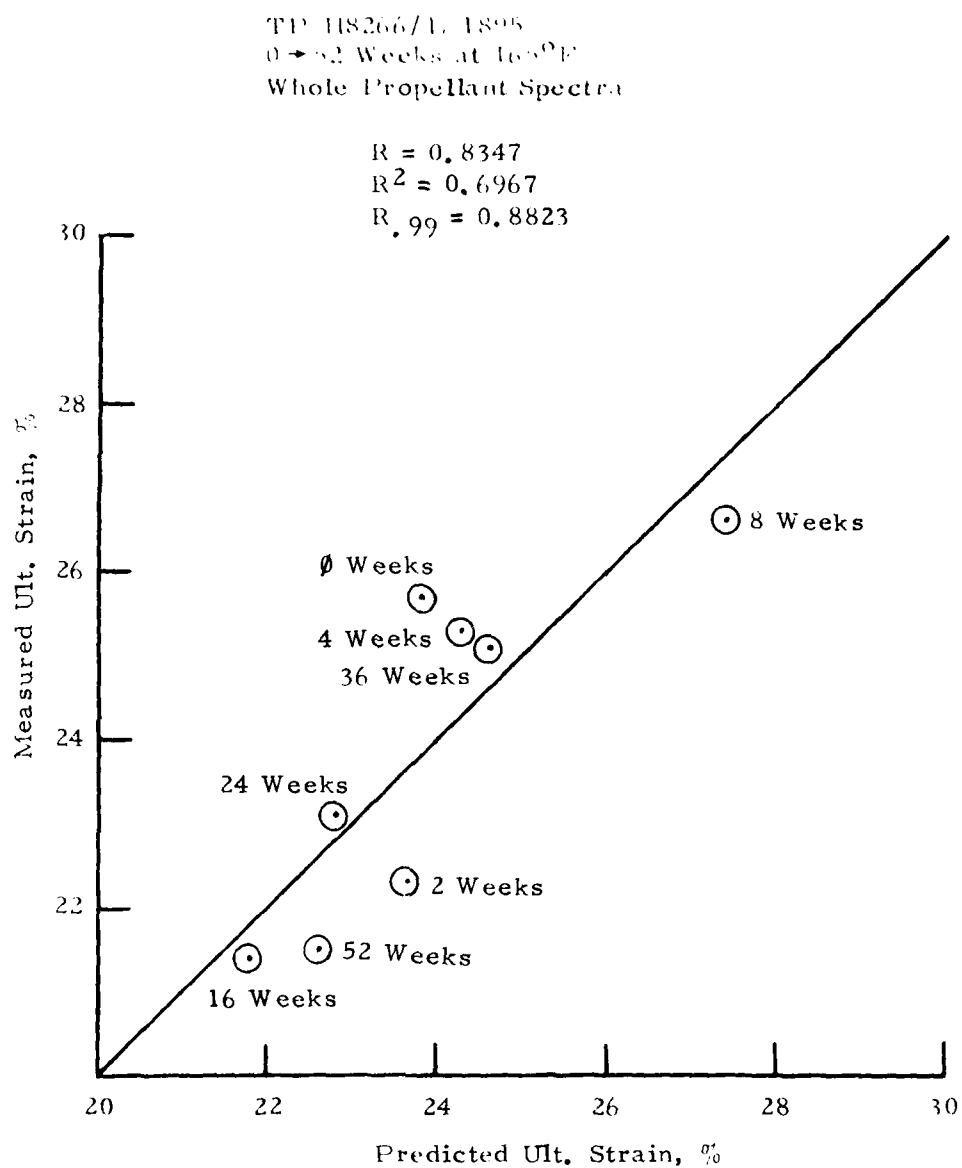
Figure F-5. Multiple Correlation for Ultimate Strain.

TP-H8266/L-1895
0 → 52 Weeks at 165°F
Whole Propellant Spectra

R = 0.7798
R^2 = 0.6081
R$_{.99}$ =
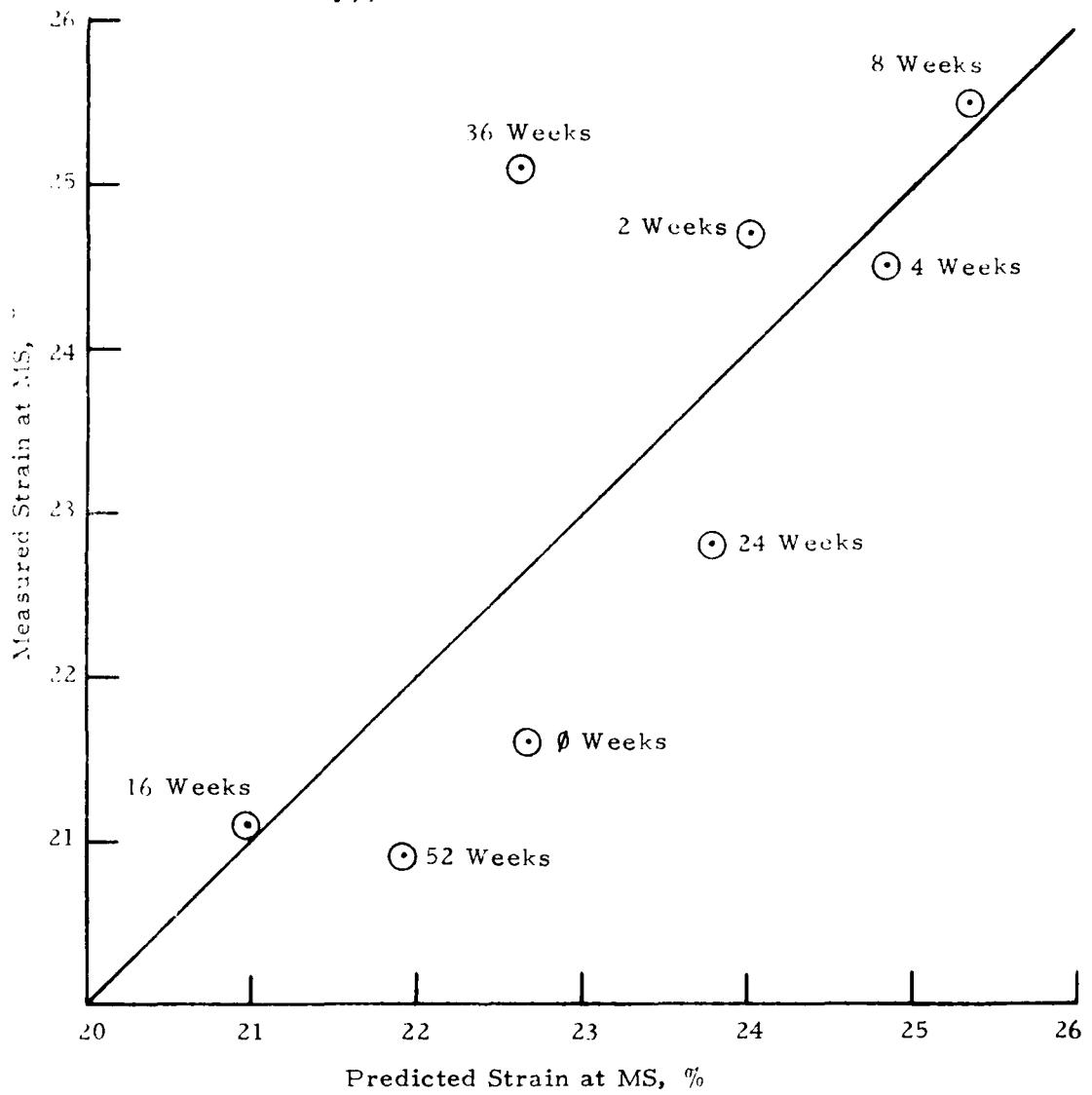
Figure F-6 Multiple Correlation for Strain at Max. Stress.

TP-118266/L-1895
0 → 52 Weeks at 165°F
Whole Propellant Spectra

R = 0.9829
R^2 = 0.9661
$R_{.99}$ =
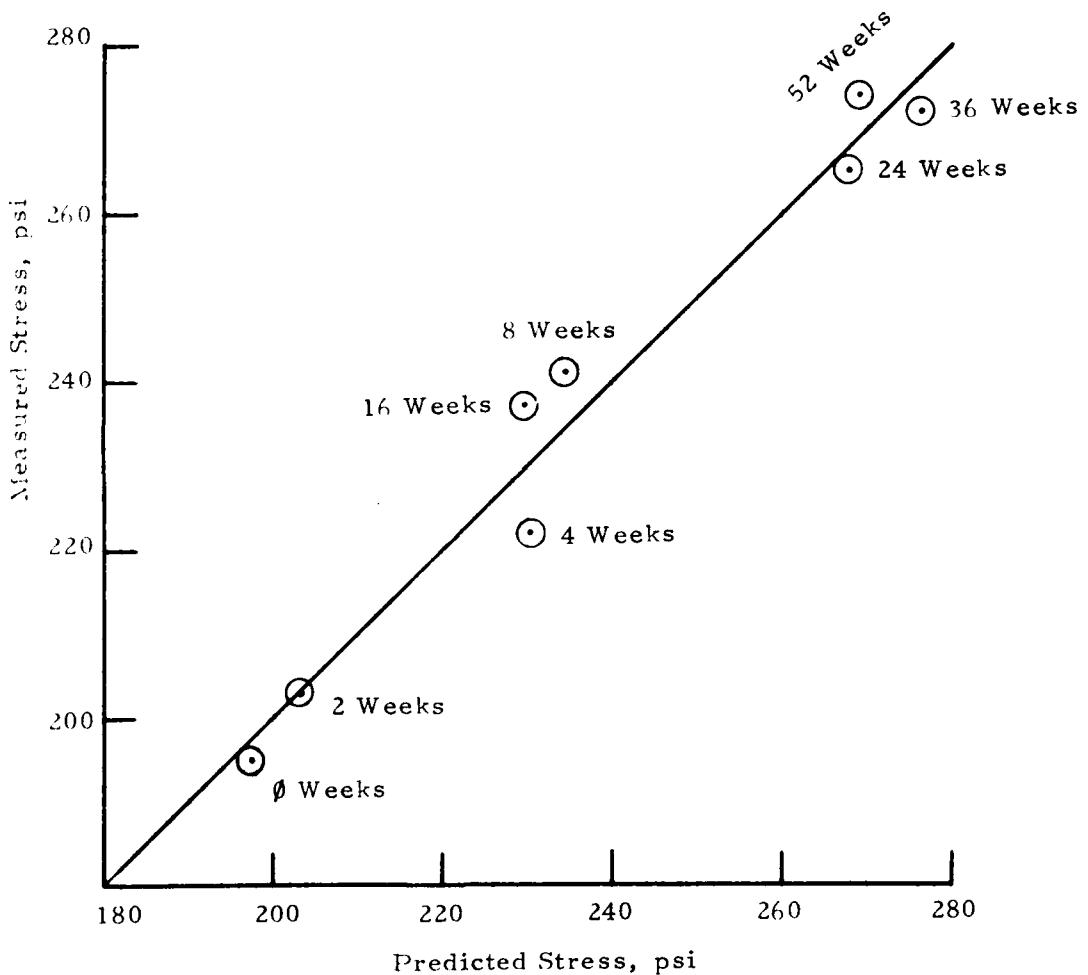
Figure F-7. Multiple Correlation for Max. Stress.

baseline; so, for normalizing, all of the spectra ended up with the same peak height at the normalizing peak, which is as was intended; however, at other peaks within this region from 2750 to 3100 wave numbers, there were shifts in the location of peaks by one resolution element, i.e., approximately eight wave numbers. The remainder of the common baseline routine uses the "NPHOTO" spectrum and selects the location of all peaks (with the exception of the normalizing peak) and freezes those wave numbers. It subsequently examines all other spectra at those wave numbers so that, if there is a wave number shift in a peak, then the peak is measured off center and a slightly diminished peak value is obtained.

All this discussion of the importance of selecting "NPHOTO" is brought out because it will be apparent when examining the results of the data reduction and statistical analysis of the propellant aged at 165°F that the correlations found are different from the correlations just reported for the propellant aged at 165°F. This wave number shift occurred because the IR spectra accumulated at the very early part of the aging of TP-H8266 propellant were not accumulated exactly as the remainder of the spectra had been acquired. These variations very clearly point out the necessity for using a standardized procedure from the beginning to the end of an aging program and show the importance of very carefully selecting that procedure so that all variables in the data acquisition method are accounted for.

Table F-3 is a list of correlations, simple and multiple, that were found for the propellant aged at 77°F. The multiple correlations are plotted on Figures F-8 through F-11. There were some very strong multiple correlations found; however, the simple correlations are not quite as strong but are statistically significant at the 95% level. Modulus of the propellant varied by only slightly more than 200 psi over the 52-week period so one would not expect to find very significant changes in the infrared spectra and the quality of the simple correlations bears out this fact.

Simple and multiple correlations found for propellant aged at 100°F are tabulated in Table F-4. As can be seen, there were some strong simple correlations... one with stress at a correlation coefficient of 0.9083 (statistically significant at the 99% confidence level). The correlation between strain at maximum stress and the peak at 1319 cm^{-1} was also statistically significant at this level. Others were significant at the 95% level. Multiple correlations found were limited to strain at maximum stress and maximum stress. Both of these correlations were statistically significant at the 99% confidence level. These correlations are plotted on Figures F-12 and F-13.

Table F-3

CORRELATIONS FOR TP-H8266/L-1895

AGED 0-52 WEEKS AT 77°F

Simple Correlations	Coefficient
Peak Height at 2931 cm^{-1} with Modulus	-0.7752
Peak Height at 2885 cm^{-1} with Ult. Strain	0.7109
Peak Height at 2885 cm^{-1} with Strain at M.S.	0.7271
Peak Height at 1651 cm^{-1} with Modulus	-0.7138

$$r_{.99} = 0.834$$
$$r_{.95} = 0.707$$

Multiple Correlations

Modulus = 3628 - 115.3(V_4)
  V_4 = Peak Height at 2931 cm^{-1}

R = 0.7751
R^2 = 0.6008
$R_{.95}$ = 0.707

Ult. Strain = -174 + 1812(V_5) - 6.983(V_8) + 0.483(V_9)
  V_5 = Peak Height at 2885 cm^{-1}
  V_8 = Peak Height at 1242 cm^{-1}
  V_9 = Peak Height at 972 cm^{-1}

R = 0.9739
R^2 = 0.9485
$R_{.99}$ = 0.962

Strain at M.S. = -65.12 + 8.476(V_5) - 3.900(V_6)
  V_5 = Peak Height at 2885 cm^{-1}
  V_6 = Peak Height at 1651 cm^{-1}

R = 0.9150
R^2 = 0.8372
$R_{.99}$ = 0.917

Max. Stress = -1076 + 147.1(V_5) - 129.6(V_8)
  V_5 = Peak Height at 2885 cm^{-1}
  V_8 = Peak Height at 1242 cm^{-1}

R = 0.9153
R^2 = 0.8378
$R_{.99}$ = 0.917

TP-H8266/L-1895
Aged 0 → 52 Weeks at 77°F
Whole Propellant Spectra

$R = 0.7751$
$R^2 = 0.6008$
$R_{.99} = 0.834$
$R_{.95} = 0.707$
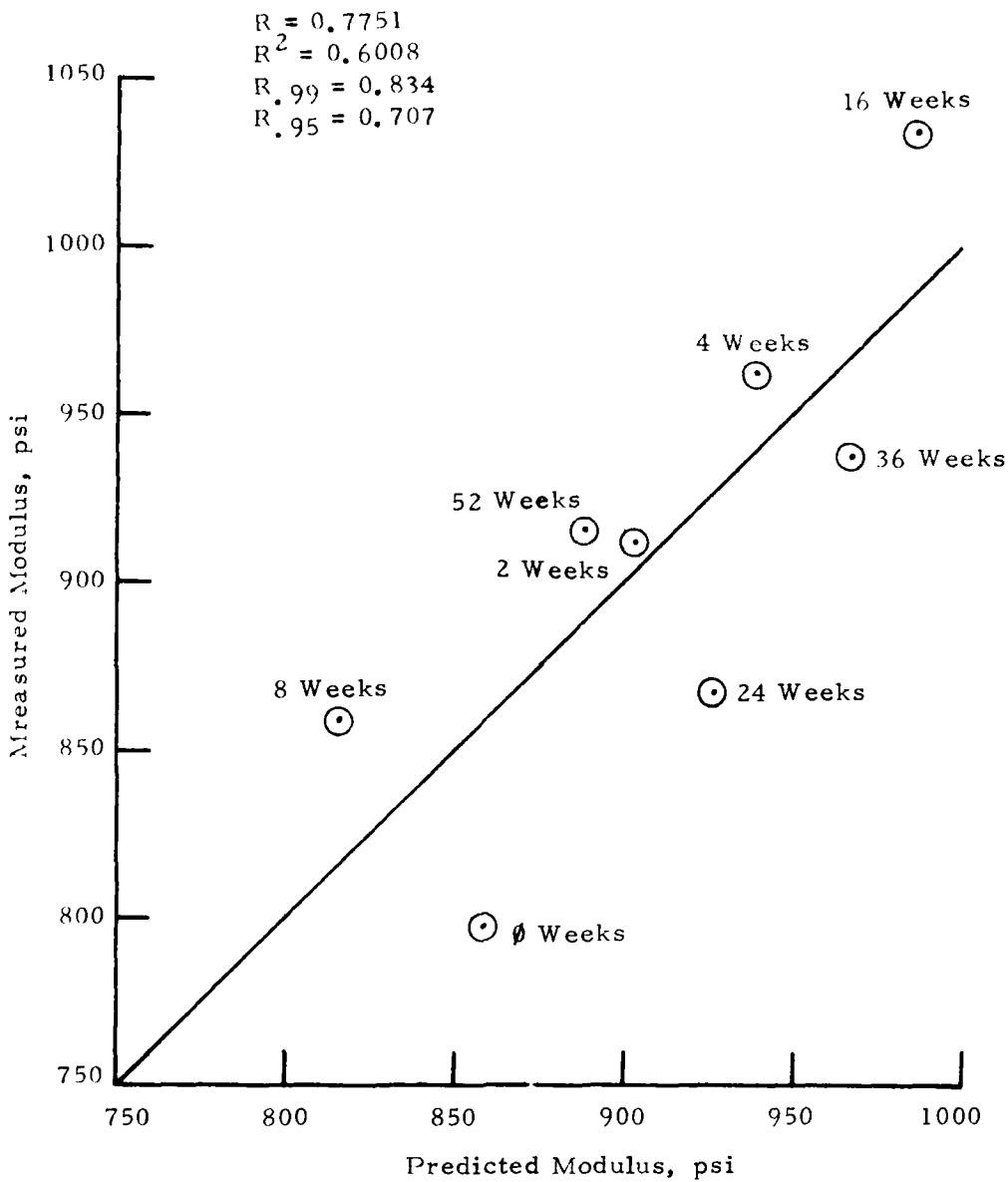
Figure F-8.   Multiple Correlation for Modulus

TP-H8266/L-1895
Aged 0 → 52 Weeks at 77°F
Whole Propellant Spectra

R = 0.9739
R² = 0.8485
R.99 =
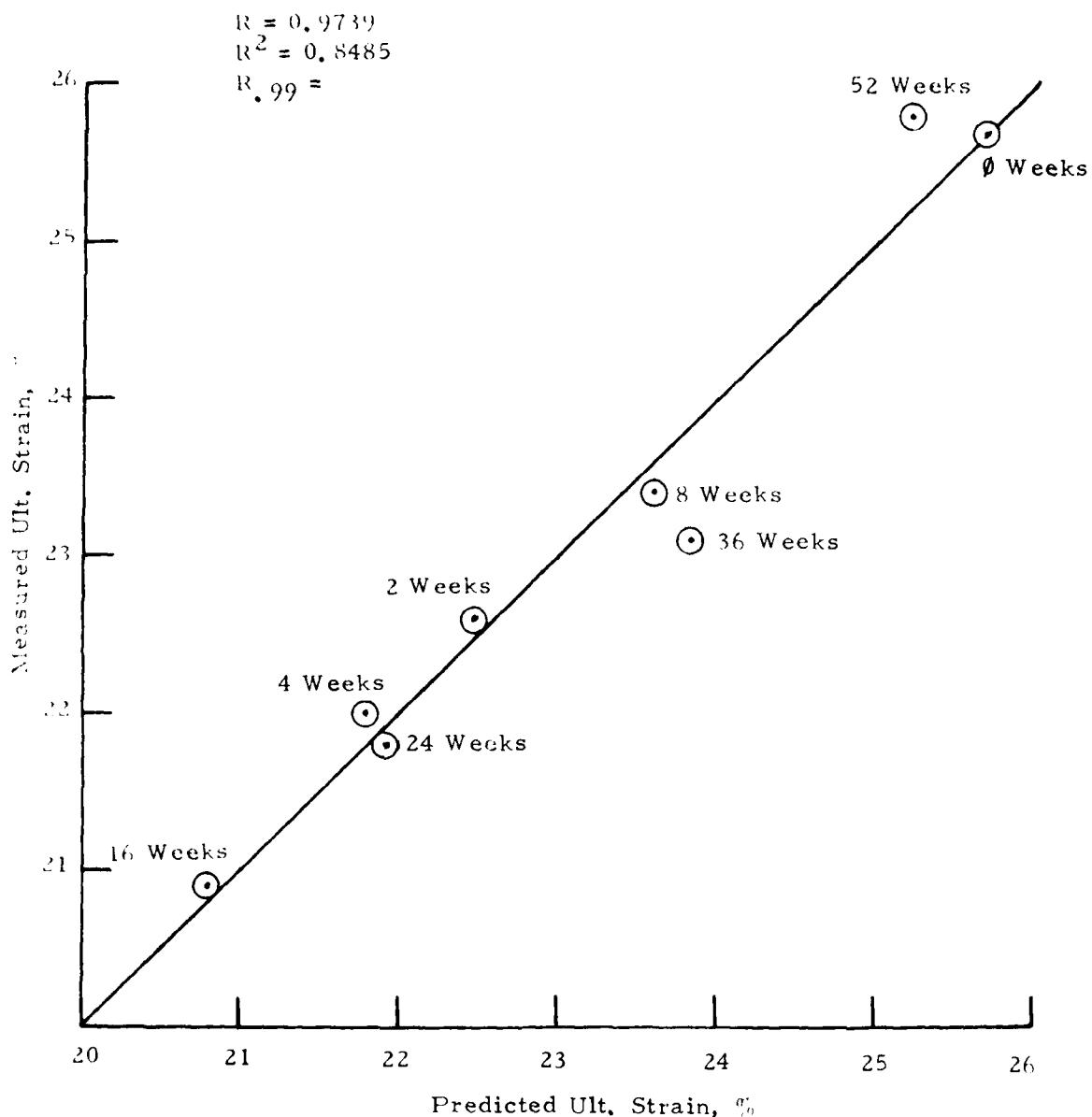
Figure F-9. Multiple Correlation for Ultimate Strain

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TP-HS266/L 1895
Aged 0→52 Weeks at 77°F
Whole Propellant Spectra

$R = 0.9150$
$R^2 = 0.8372$
$R_{.99} = 0.917$
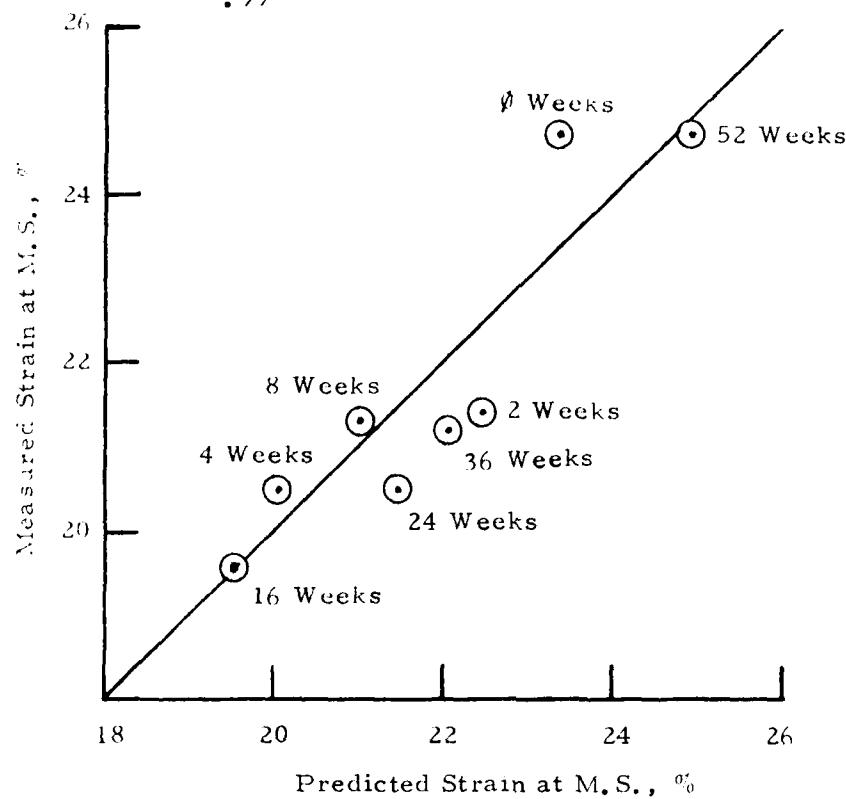
Figure F-10. Multiple Correlation for Strain at M.S.

TP-H8266/L-1895
Aged 0→52 Weeks at 77°F
Whole Propellant Spectra

$R = 0.9153$
$R^2 = 0.8378$
$R_{.99} = 0.917$
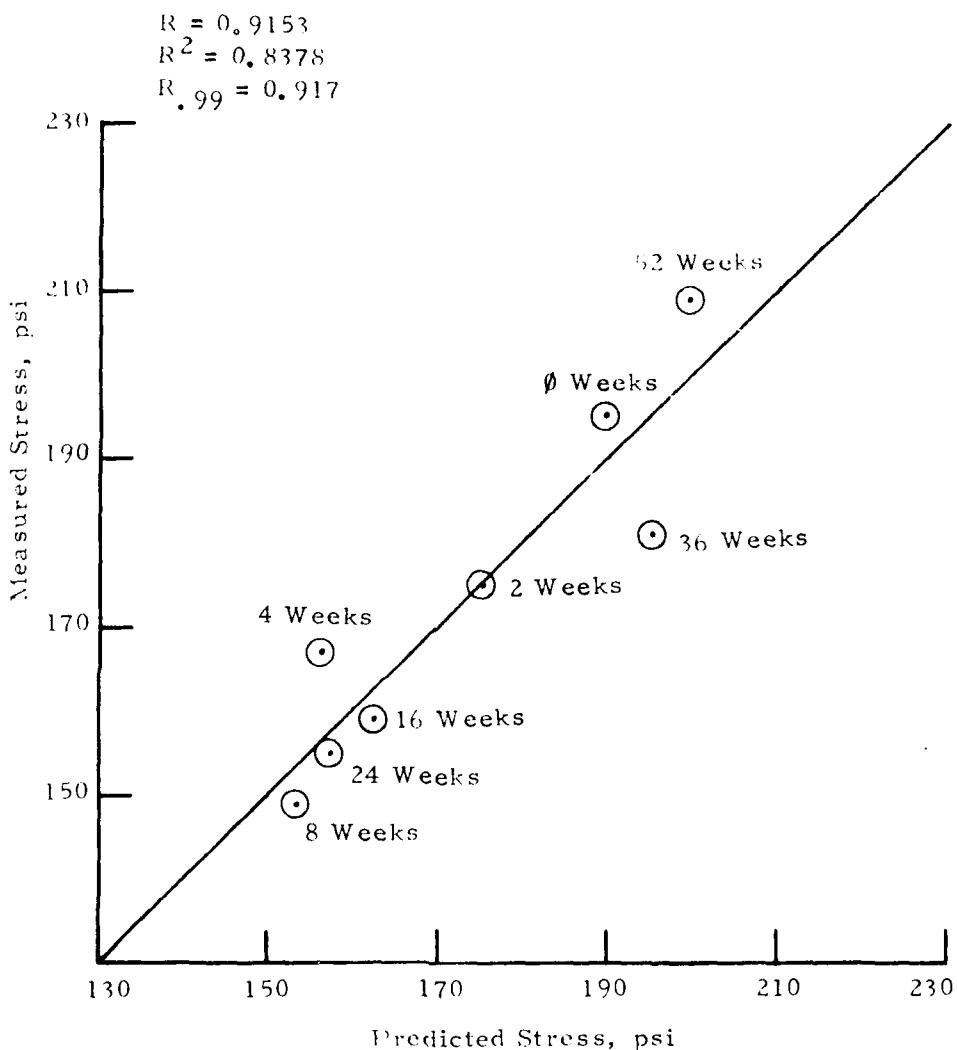
Figure F-11. Multiple Correlation for Maximum Stress

Table F-4

CORRELATIONS FOR TP-H8266/L-1895

AGED 0-52 WEEKS AT 100°F

Simple Correlations	Coefficient
Peak Height at 2962 cm^{-1} with Stress	0.9083
Peak Height at 2931 cm^{-1} with Strain at MS	0.7333
Peak Height at 2885 cm^{-1} with Stress	0.8252
Peak Height at 1319 cm^{-1} with Strain at MS	0.8479
Peak Height at 1242 cm^{-1} with Strain at MS	0.7381

$$r_{.99} = 0.834$$
$$r_{.95} = 0.707$$

Multiple Correlations

Modulus - None

Ultimate Strain - None

Strain at M.S. $= -70.60 + 3.283(V_4) + 19.44(V_7)$
$\quad V_4$ = Peak Height at 2931 cm^{-1}
$\quad V_7$ = Peak Height at 1319 cm^{-1}

$R = 0.9310$
$R^2 = 0.8668$
$R_{.99} = 0.917$

Max. Stress $= -525.2 + 45.32(V_3)$
$\quad V_3$ = Peak Height at 2962 cm^{-1}

$R = 0.9084$
$R^2 = 0.8252$
$R_{.99} = 0.834$

TP-H8266/ L-1895
Aged 0 - 52 at 100°F
Whole Propellant Spectra

$R = 0.9310$
$R^2 = 0.8668$
$R_{.99} = 0.917$
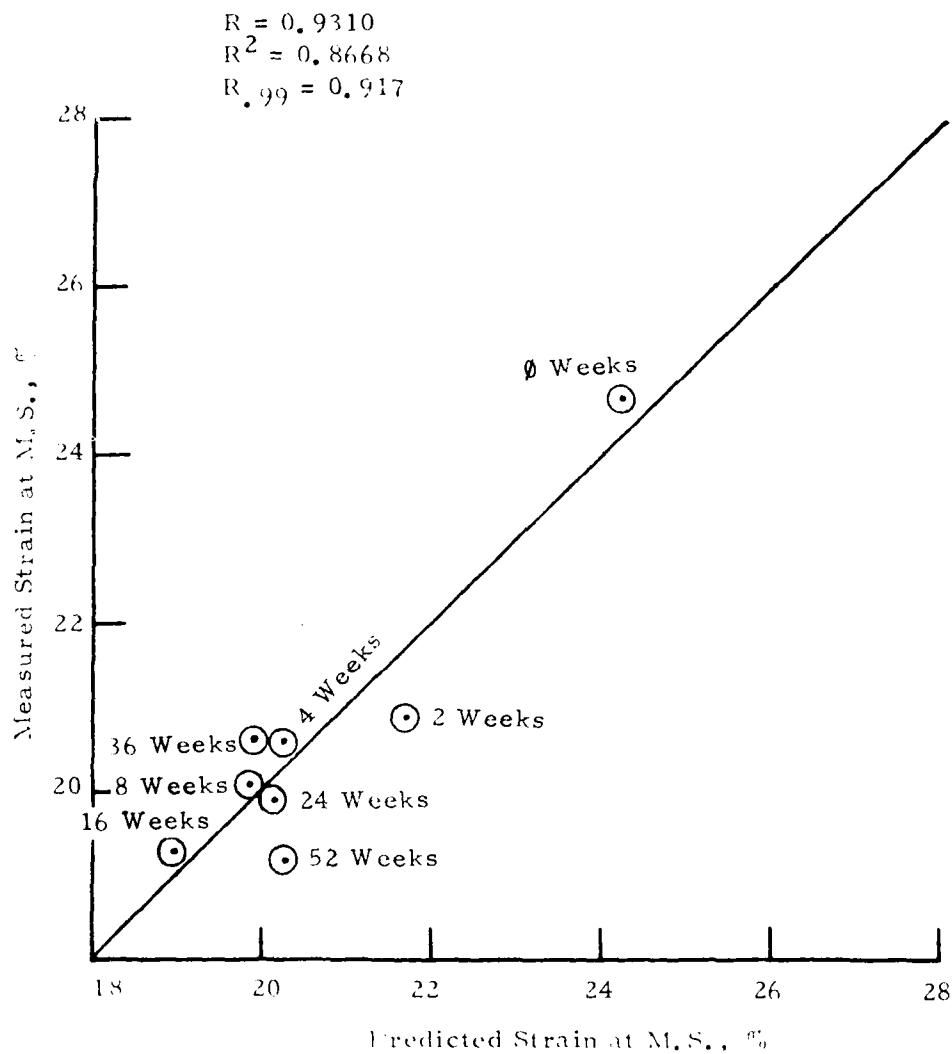
Figure F-12. Multiple Correlations for Strain at M.S.

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TP-H82266/L-1895
Aged 0→52 Weeks at 100°F
Whole Propellant Spectra

R = 0.9084
R^2 = 0.8252
$R_{.99}$ = 0.834
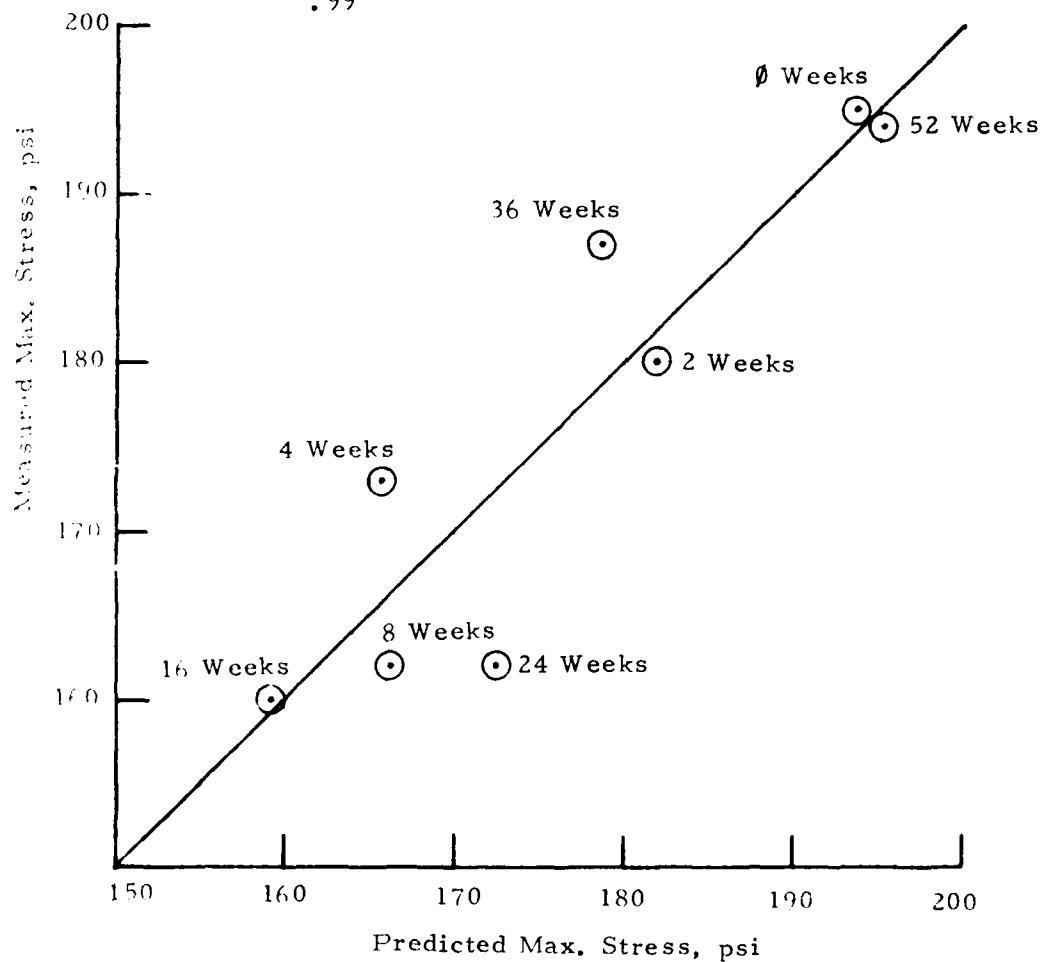
Figure F-13.   Multiple Correlation for Max. Stress

Treatment of propellant aged at 145°F produced only one simple correlation and one multiple correlation. This is shown in Table F-5, and the multiple correlation is plotted on Figure F-14. On Figure F-14 note that there is no consistent progression of maximum stress with time as the propellant ages, but that the maximum stress value for the propellant vary considerably at each test point. Still the multiple correlation equation did account for this, and this shows that the peak heights are varying as the structure of the propellant changes with time at that aging temperature. The fact that very few correlations were found is perhaps indicative of the complexity of the aging taking place at that temperature. At the two lower temperatures, 77 and 100°F, there were more correlations, indicative of the fact that there are fewer aging reactions proceeding and those few reactions are controlling the mechanical properties of the propellant. At 145°F aging this may not be true. The reactions may be more complex and may be changing from time period to time period so that it is more difficult to identify those reactions simply by looking in the infrared.

Propellant aged at 165°F showed a large number of correlations, both simple and multiple. Four simple correlations were revealed, two of which were significant at the 99% confidence level, and two significant at the 95% confidence level. Now referring back to Table F-2, which is the same data reduced in a slightly different manner, we find that for the simple correlations all four of the peak heights shown on Table F-6 are also on Table 2, thus even with the slightly different data reduction method, the correlations still appear and the value of the coefficient remains approximately the same. The peak at 3016 cm^{-1} shown on Table F-6 is in reality the same peak as shown on Table F-2 as 3009 cm^{-1}. This is the slight shift in peak location that was discussed earlier. There is one rather astonishing thing revealed by comparison of these two tables, and that is the sign of the correlation that occurred with stress and the 3016 cm^{-1} peak in Table F-6. That same peak shown in Table F-2 has an opposite sign. There is no explanation for this. Looking now at the multiple correlations for propellant aged at 165°F, we see that for modulus there is one peak involved (3016 cm^{-1}); while on Table F-2, we find that there two peaks involved in the modulus correlation, the peak at 3009 and the one at 1319 cm^{-1}. On Table F-6 this correlation coefficient is slightly less than the corresponding one on Table F-2. This correlation for modulus is plotted on Figure F-15 and a comparison with Figure F-7 will reveal that the correlation is not nearly so strong on Figure F-15. Correlations for ultimate strain (Table F-6) reveal that the same two peaks were involved here as were involved in the correlation listed in Table F-2. Correlation listed for strain at maximum stress dropped out completely for this set of data while there was a correlation, albeit not very strong, for the data displayed in Table F-2. The stress equation in Table F-6 includes only one peak height and its correlation coefficient is quite high being significant at the 99% confidence level. Looking at the stress equation on Table F-2, the same peak is involved; however, there are two more variables included in that equation and while the correlation coefficient shown in Table F-2 is slightly higher, the fact that there are now four terms in that equation reduces somewhat the confidence that one would place in that equation.

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Table F-5

<u>CORRELATIONS FOR TP-H8266/L-1895</u>

<u>AGED 0-52 WEEKS AT 145°F</u>

<u>Simple Correlations</u>

Peak Height at 3016 cm^{-1} with Strain at M.S.

$R = -.7892$

$R_{.99} = 0.834$

$R_{.95} = 0.707$

<u>Multiple Correlations</u>

Modulus - None

Ultimate Strain - None

Strain at M.S. - None

Stress $= 509.6 - 208.8(V_2) + 42.99(V_3)$
    $V_2 =$ Peak Height at 3016 cm^{-1}
    $V_3 =$ Peak Height at 2962 cm^{-1}

$R = 0.9393$

$R^2 = 0.8823$

$R_{.99} = 0.917$

TP-H8266/L-1895
Aged 0→62 Weeks at 145°F
Whole Propellant Spectra

R = 0.9393
R² = 0.8823
R.99 = 0.917
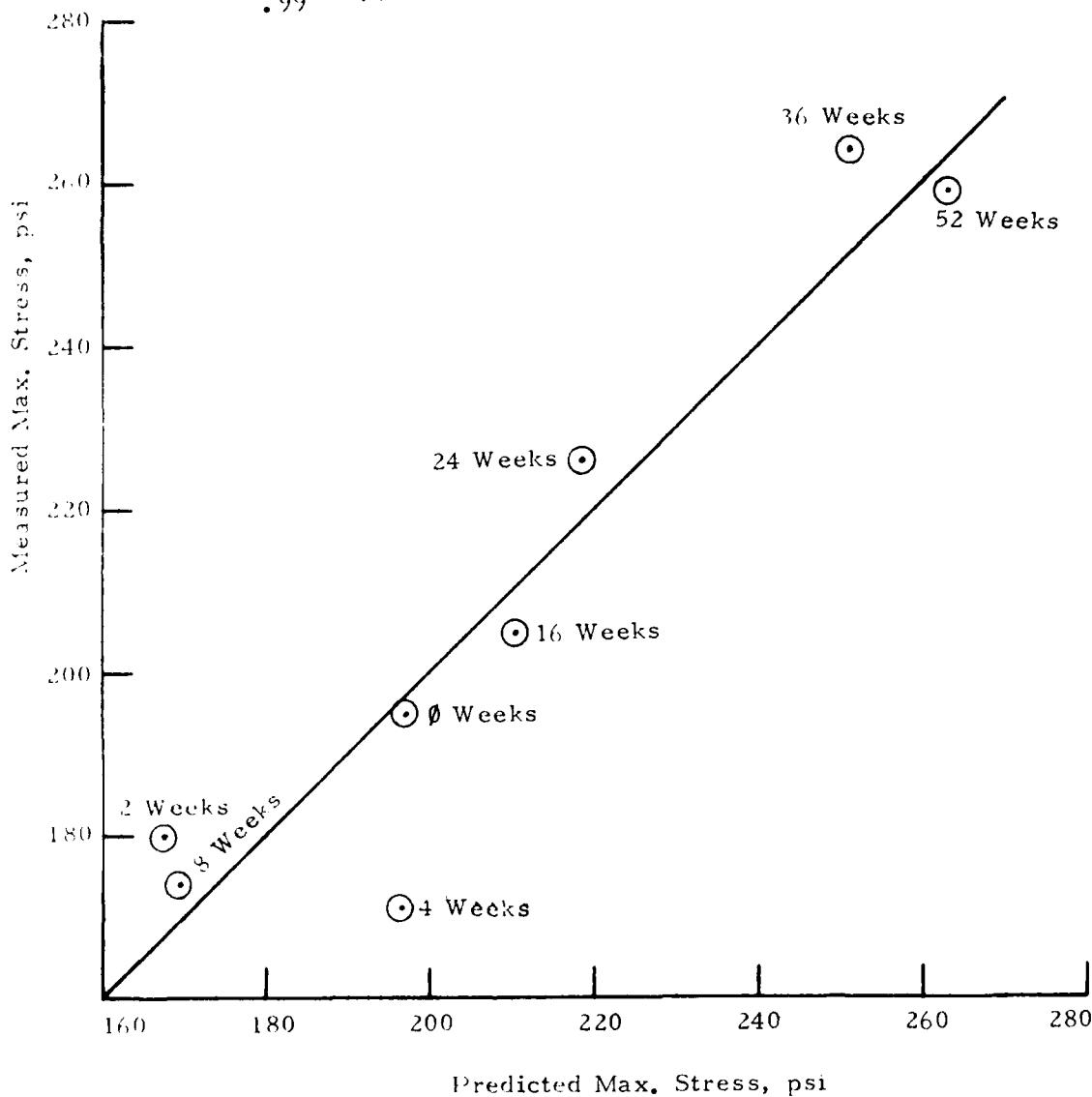

Figure F-14. Multiple Correlation for Maximum Stress

CORRELATIONS FOR TP-H8266/L-1895

AGED 0-52 WEEKS AT 165°F

Simple Correlations	Coefficient
Peak Height at 3016 cm^{-1} with Modulus	-0.8682
Peak Height at 3016 cm^{-1} with Stress	0.9594
Peak Height at 2885 cm^{-1} with Stress	0.7069
Peak Height at 1651 cm^{-1} with Stress	-0.7490

$$r_{.99} = 0.834$$
$$r_{.95} = 0.707$$

Multiple Correlations

Modulus = 8462 - 1571(V_2)

    V_2 = Peak Height at 3016 cm^{-1}

R = 0.8682
R^2 = 0.7538
$R_{.99}$ = 0.834

Ultimate Strain = -25.01 + 1.233(V_9) + 8.991(V_{11})

    V_9 = Peak Height at 972 cm^{-1}

    V_{11} = Peak Height at 779 cm^{-1}

R = 0.8348
R^2 = 0.6969
$R_{.99}$ = 0.917
$R_{.95}$ = 0.836

Strain at M.S. - None

Stress = 1135 - 195.1(V_2)

    V_2 = Peak Height at 3016 cm^{-1}

R = 0.9594
R^2 = 0.9204
$R_{.99}$ = 0.834

The three multiple correlations found for the 165°F aging are plotted in Figures F-15, F-16, and F-17.

These data for TP-H8266 were treated in one other way. We took all of the IR spectra and all of the mechanical property data for the 145°F aging and the 165°F aging, combined them, and treated them statistically so that the number of observations was increased from 8 to 16. We also considered this as a test of whether the aging reactions occurring at 165°F were also the same aging reactions occurring at 145°F. If correlations could be found and if the correlations were strong, then that must be a good indication that the aging chemistry at 145°F is closely akin to that occurring at 165°F. If correlations that had been present when the two sets of aging data were treated separately vanished when they were combined, then that is a strong indication that the chemistries of aging at the two temperatures are different. Correlations that were found by this treatment of the data are displayed in Table F-7. Simple correlations are shown at the top of the table and some were statistically valid at the 99.9% level; the remainder were significant at the 99% level. Notice, however, that the correlations involved only modulus and stress. Neither strain measurement correlated. As would be expected from the simple correlations, only two multiple correlations were found, one with modulus and one with stress. Both of these correlations are statistically significant at the 99% level; however, the stress correlation is considerably stronger than the modulus correlation. These two correlations are plotted in Figures F-18 and F-19.

From the fact that the correlations concerning strain were totally absent, and there had been a strain correlation for propellant aged at 165°F and not for propellant aged at 145°F, we can surmise that the reactions governing strain are different at the two aging temperatures but that the chemical reactions governing stress are probably the same and just proceed at different rates at the different temperatures. Examination of Figure F-19 reveals that generally the 145°F age temperatures are grouped at the lower end of the plot while the values concerning stress at 165°F aging are generally grouped at the top of the plot. The same observation can be made concerning the modulus plot (Figure F-18).

CONCLUSIONS

1) Computer program E490 for IR data reduction works quite well, and at near the maximum number of spectra that it is capable of handling, it performs the data reduction in less than five minutes.

2) The statistical data analysis program works well and successfully reduced all of the statistical data presented.

TP-H8266/L-1895
Aged 0→52 Weeks at 165°F
Whole Propellant Spectra

R = 0.8682
R^2 = 0.7538
$R_{.99}$ = 0.834
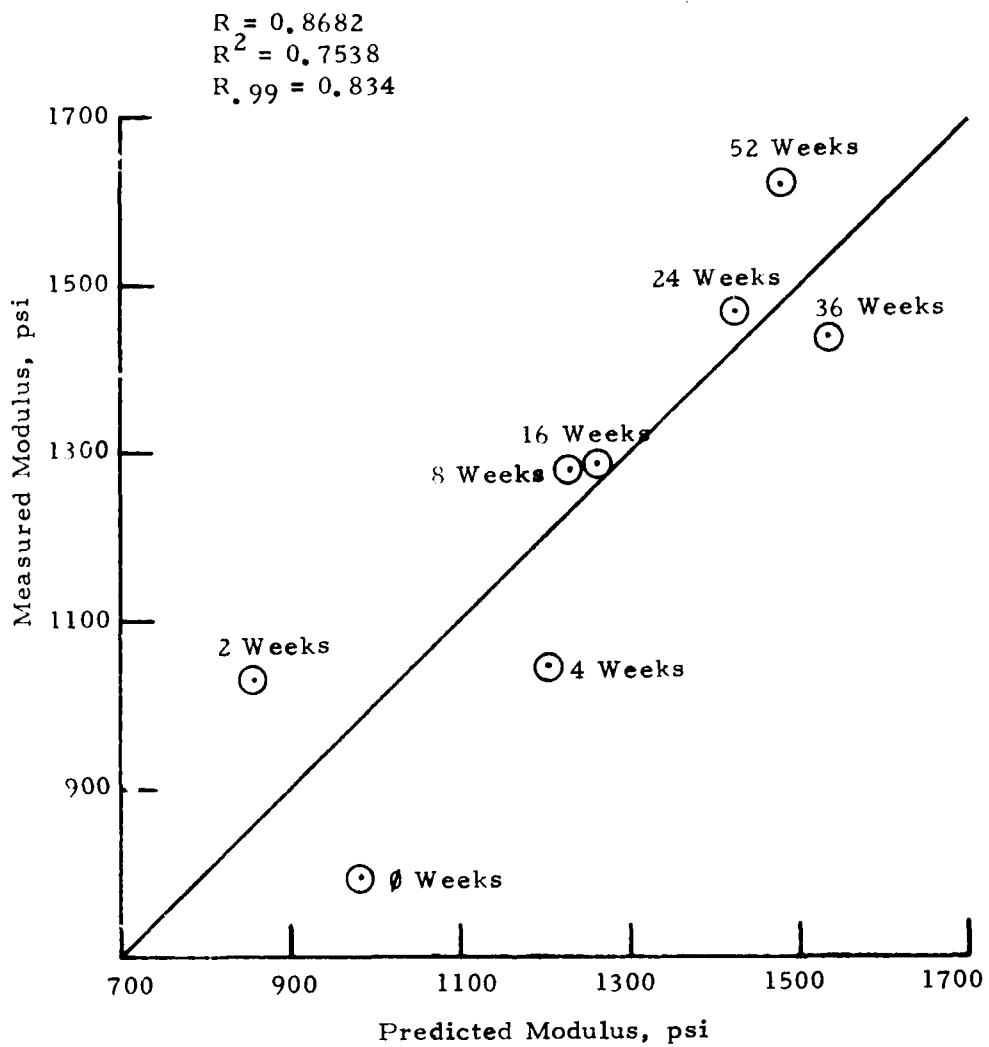
Figure F-15. Multiple Correlation for Modulus

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TP-H8266/L-1895
Aged 0→52 Weeks at 165°F

R = 0.8348
R^2 = 0.6969
$R_{.95}$ = 0.836
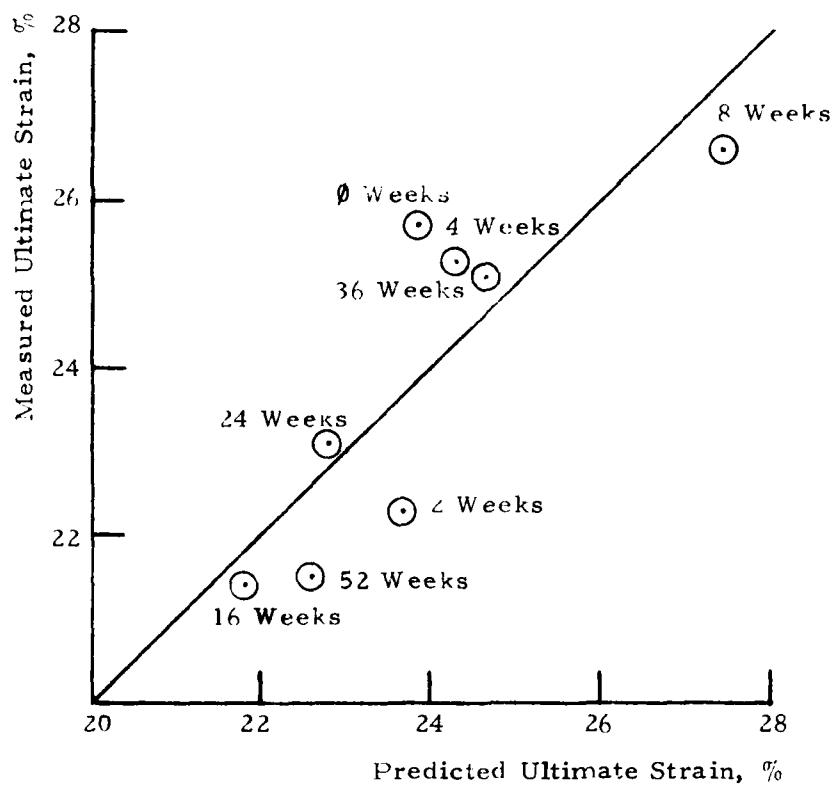
Figure F-16. Multiple Correlation for Ultimate Strain
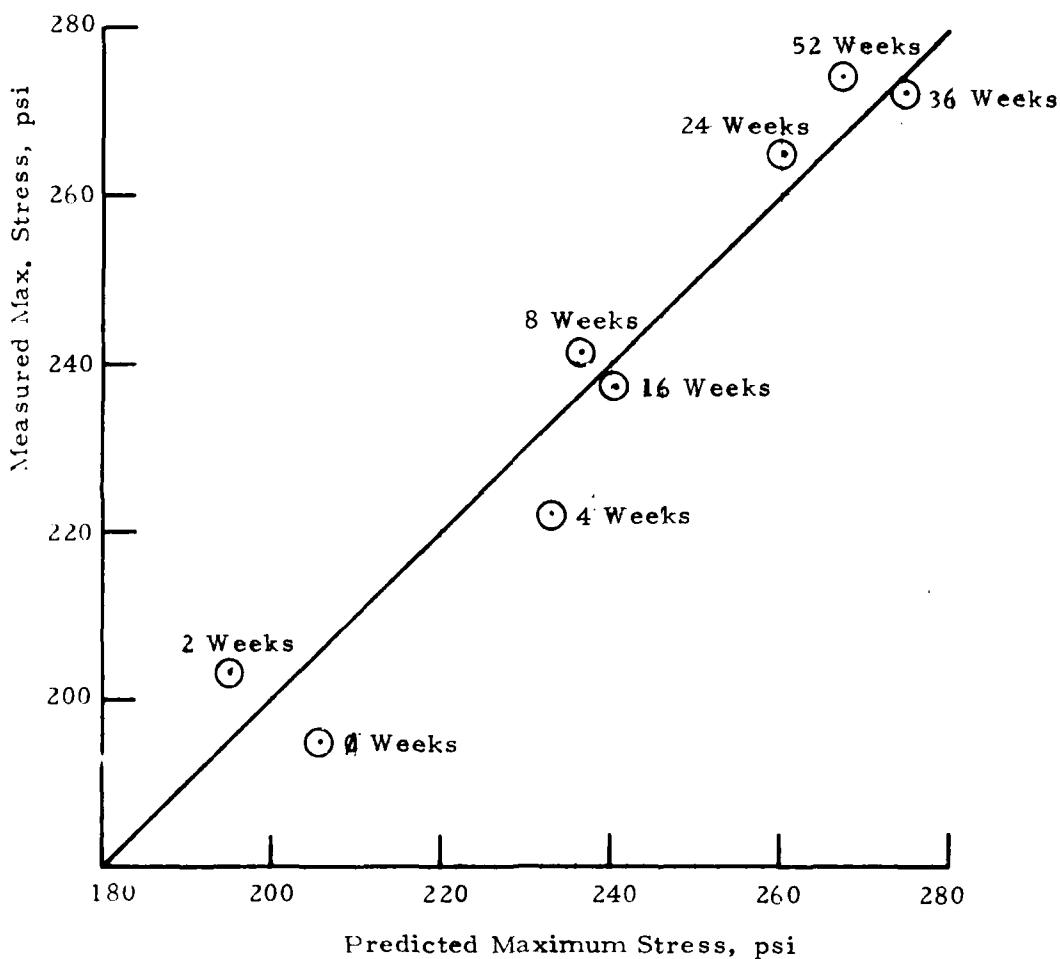
Figure F-17. Multiple Correlation for Maximum Stress

Table F-7

<u>CORRELATIONS FOR TP-H8266/L-1895</u>

<u>AGED $\emptyset$-52 WEEKS AT 145° AND 165°F</u>

(Combined Data Sets for the Two Aging Conditions)

<u>Simple Correlations</u>	<u>Coefficient</u>
Peak Height at 3016 cm^{-1} with Modulus	-0.7957
Peak Height at 3016 cm^{-1} with Stress	-0.8214
Peak Height at 2885 cm^{-1} with Stress	0.7289
Peak Height at 1651 cm^{-1} with Modulus	-0.6726
Peak Height at 1651 cm^{-1} with Stress	-0.6919
Peak Height at 1319 cm^{-1} with Modulus	-0.6997

$$r_{.999} = 0.742$$
$$r_{.99} = 0.623$$

<u>Multiple Correlations</u>

$\text{Modulus} = 2835 - 860.6(V_2) + 221.3(V_3) - 1672(V_7)$ $R = 0.9163$
$V_2 = \text{Peak Height at 3009 cm}^{-1}$ $R^2 = 0.8396$
$V_3 = \text{Peak Height at 2963 cm}^{-1}$ $R_{.99} = 0.773$
$V_7 = \text{Peak Height at 1319 cm}^{-1}$

Ultimate Strain - None
Strain at M.S. - None

$\text{Stress} = -606 - 95.11(V_2) + 100.1(V_5) - 236.3(V_7) + 85.42(V_8)$
$V_2 = \text{Peak Height at 3016 cm}^{-1}$
$V_5 = \text{Peak Height at 2885 cm}^{-1}$ $R = 0.9754$
$V_7 = \text{Peak Height at 1319 cm}^{-1}$ $R^2 = 0.9516$
$V_8 = \text{Peak Height at 1242 cm}^{-1}$ $R_{.99} = 0.821$

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TP-H8266/L-1895
Aged 0 → 52 Weeks at 145° and 165°F
Whole Propellant Spectra

R = 0.9163
R^2 = 0.8396
$R_{.99}$ = 0.773
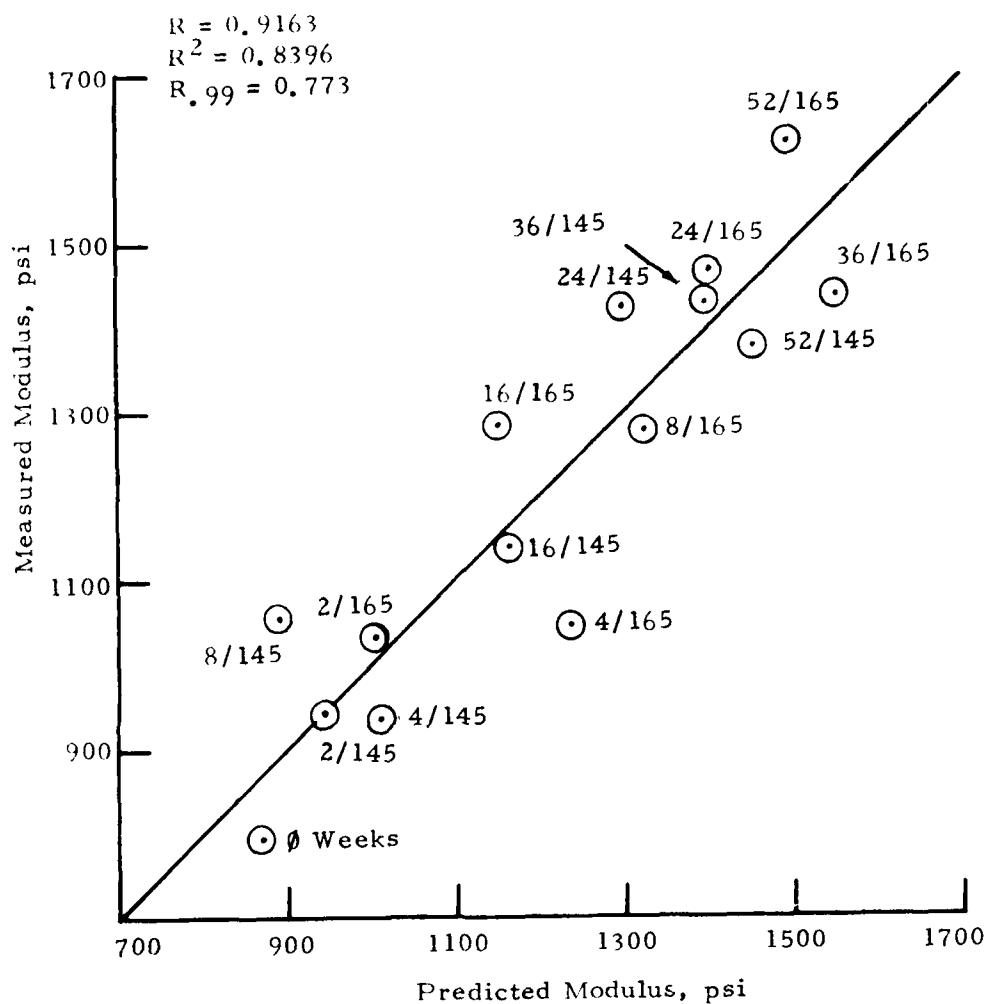
Figure F-18.   Multiple Correlation for Modulus
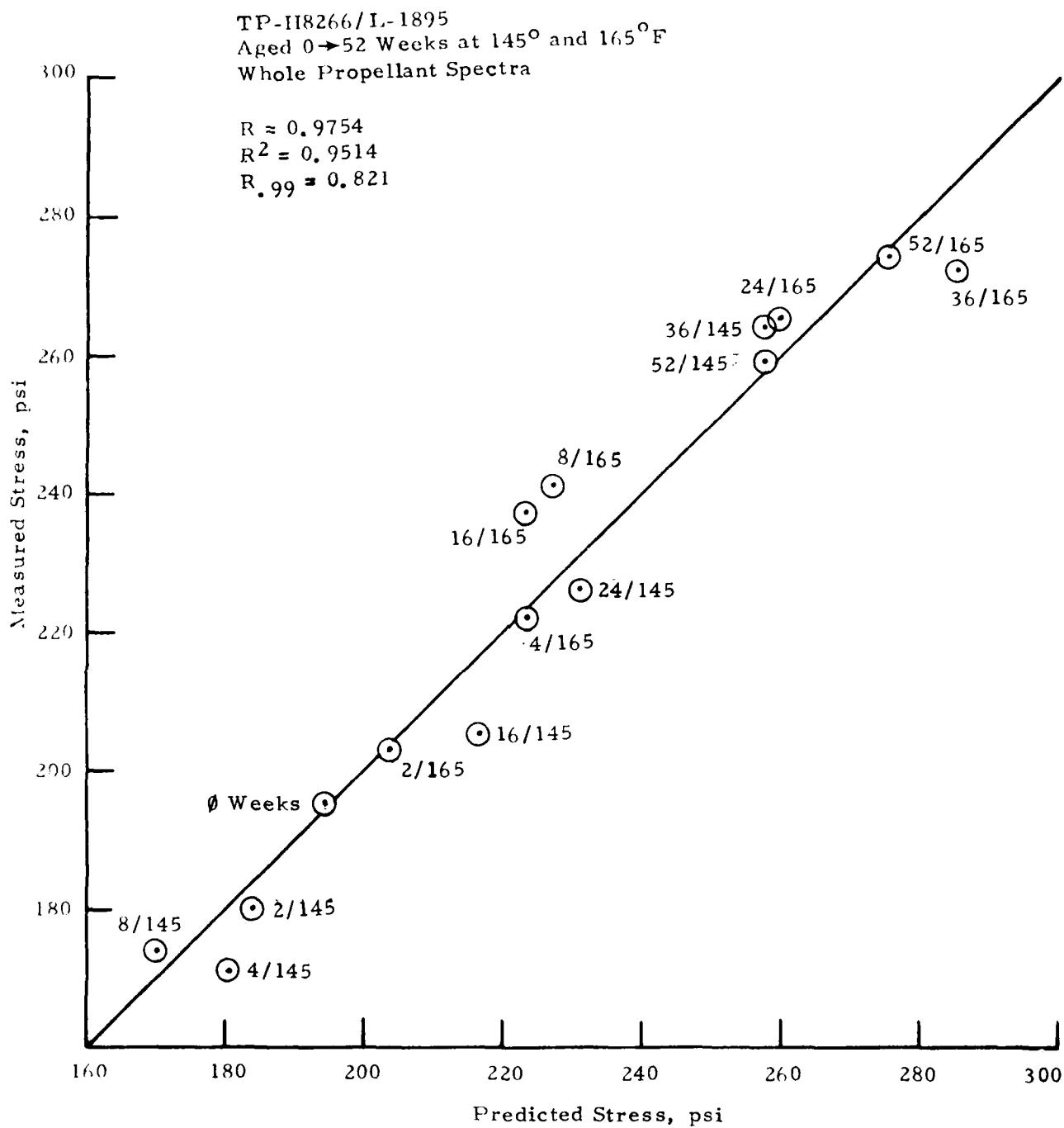
Figure F-19. Multiple Correlation for Maximum Stress

3) Subtle differences in the IR data reduction procedures do not completely destroy the simple correlations, but they do, however, introduce new correlations and do eliminate other correlations. These subtle differences do change multiple correlations.

4) Multiple correlations reveal something of the chemistry of aging and may be valuable for the prediction of age life.

5) The simple correlations reveal quite a bit about the chemistry of aging and will be useful in predicting age life.

6) The data variations that were found indicate a very strong need for a study of the reproducibility of the method by which the IR data are acquired.

APPENDIX G

CORRELATIONS OF IR PEAK HEIGHT CHANGES

AND PROPELLANT MECHANICAL PROPERTY

CHANGES FOR TP-H8278 PROPELLANT

WHOLE PROPELLANT

Mechanical property data from the aging of TP-H8278 propellant, Mix W-65, showed that propellant being aged at 145° and $165^\circ F$ was undergoing the greatest amount of change with the parameters modulus and maximum stress showing increases with time. Infrared spectra of whole propellant for each of the test intervals was reduced by computer and peak heights tabulated.

Data for the propellant aged 16 weeks at the four temperatures, 77°, 100°, 145°, and $165^\circ F$, were treated so that changes in peak height could be compared against changes in mechanical properties. Table G-1 is a list of the correlation coefficients calculated for changes in peak height at selected wave numbers and the two mechanical properties, maximum stress and modulus.

Correlation coefficients calculated for changes in peak height and maximum stress and modulus showed that there were four peaks in the infrared spectrum of the propellant which correlated with maximum stress and modulus. These peaks occurred at 3084, 2852, 1514, and 1313 cm^{-1}. As can be seen in Table G-1, with only four data points a correlation coefficient of .9 is required for a 90% confidence level. The peak occurring at 3084 cm^{-1} underwent very small changes and those changes were not considered to be of sufficient magnitude for an accurate correlation with stress and modulus. The peak occurring at 1313 cm^{-1} had a high correlation coefficient for stress and modulus and a plot of these data is given on Figure G-1. Other correlations were not considered to be valid in light of the necessity for a .9 correlation coefficient to achieve a confidence level of 90%.

For propellant aged at $165^\circ F$, there were 9 data points and a correlation coefficient of 0.582 was required for a 90% confidence level. The spectral peak at 1646 cm^{-1} had high correlation coefficients with both maximem stress and modulus. These data are plotted on Figure G-2.

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TABLE G-1

CORRELATION COEFFICIENTS (TP-H8278/W-65)

| Wave No.	Aged 16 wk. at various temp.		Aged at 165°F for various times		Aged at 145°F for various times	
	Max. Stress	Modulus	Max. Stress	Modulus	Max. Stress	Modulus
3084	-0.9374	-0.9530	-0.3629	-0.2284	-0.7483	-0.5611
3006	0.7809	0.8247	0.6903	0.5368	-0.2977	0.1770
2852	-0.8026	-0.7659	-0.4357	-0.6090	-0.0829	
1646	-0.3222	-0.2462	-0.7631	-0.8404	-0.8468	-0.8993
1514	-0.8595	-0.8012	-0.5829	-0.3831	-0.4073	-0.3454
1313	-0.9840	-0.9568	-0.6456	-0.6738	-0.3973	
1236	-0.3322	-0.3084	-0.7058	-0.6675	-0.1773	
965	-0.0279	-0.0280	-0.0238		0.9374	0.7670
911	0.2714	0.2705	0.0230		0.8229	0.6673
772	0.1192	0.1867	-0.3904		-0.2204	
No. Data Points	4		9		7	
Significant Value at 90% Confidence	.9		.582		.669	

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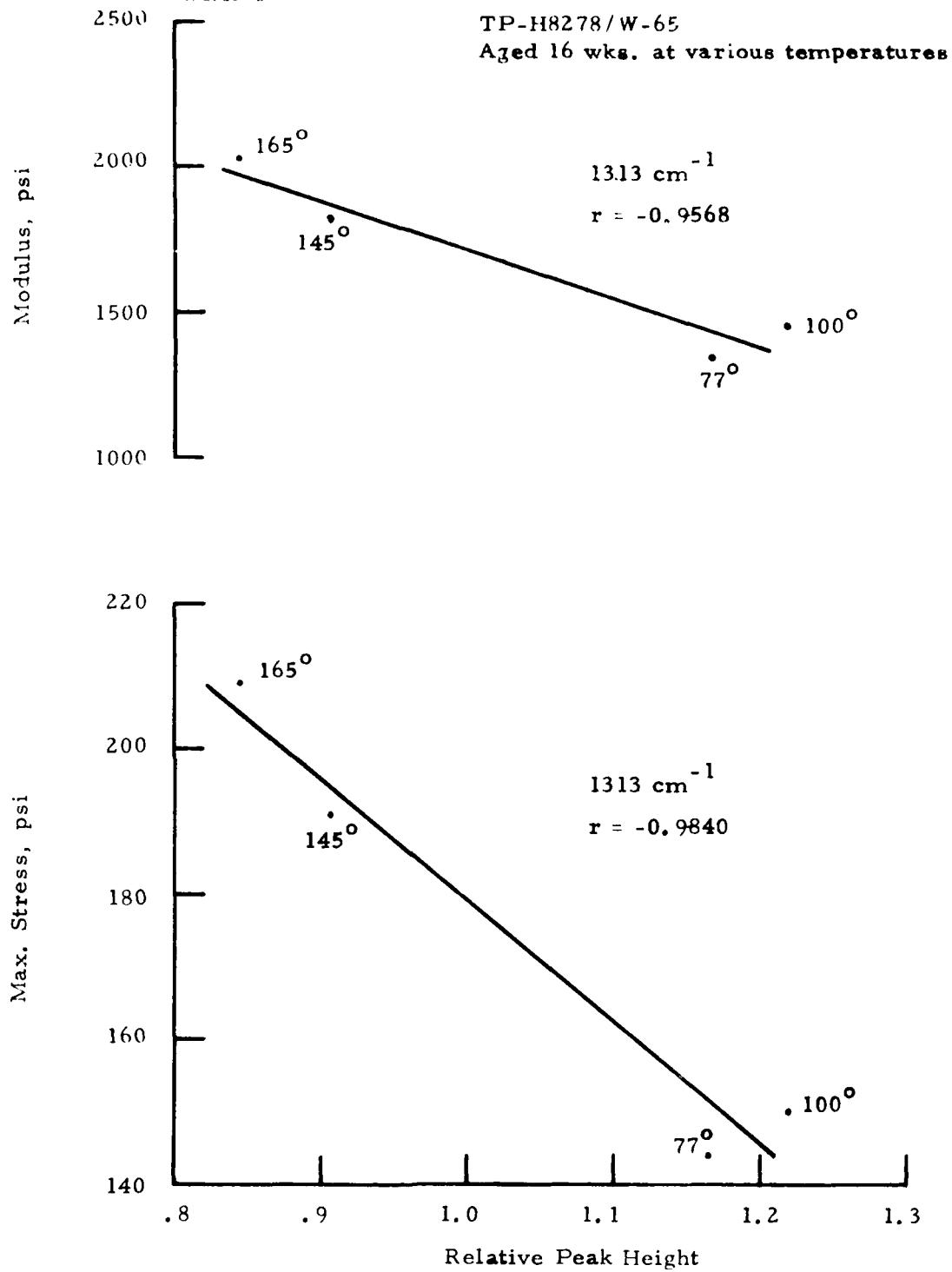
Figure G-1.   Correlation of Stress and Modulus with
Peak Height Changes at 1313 cm^{-1}

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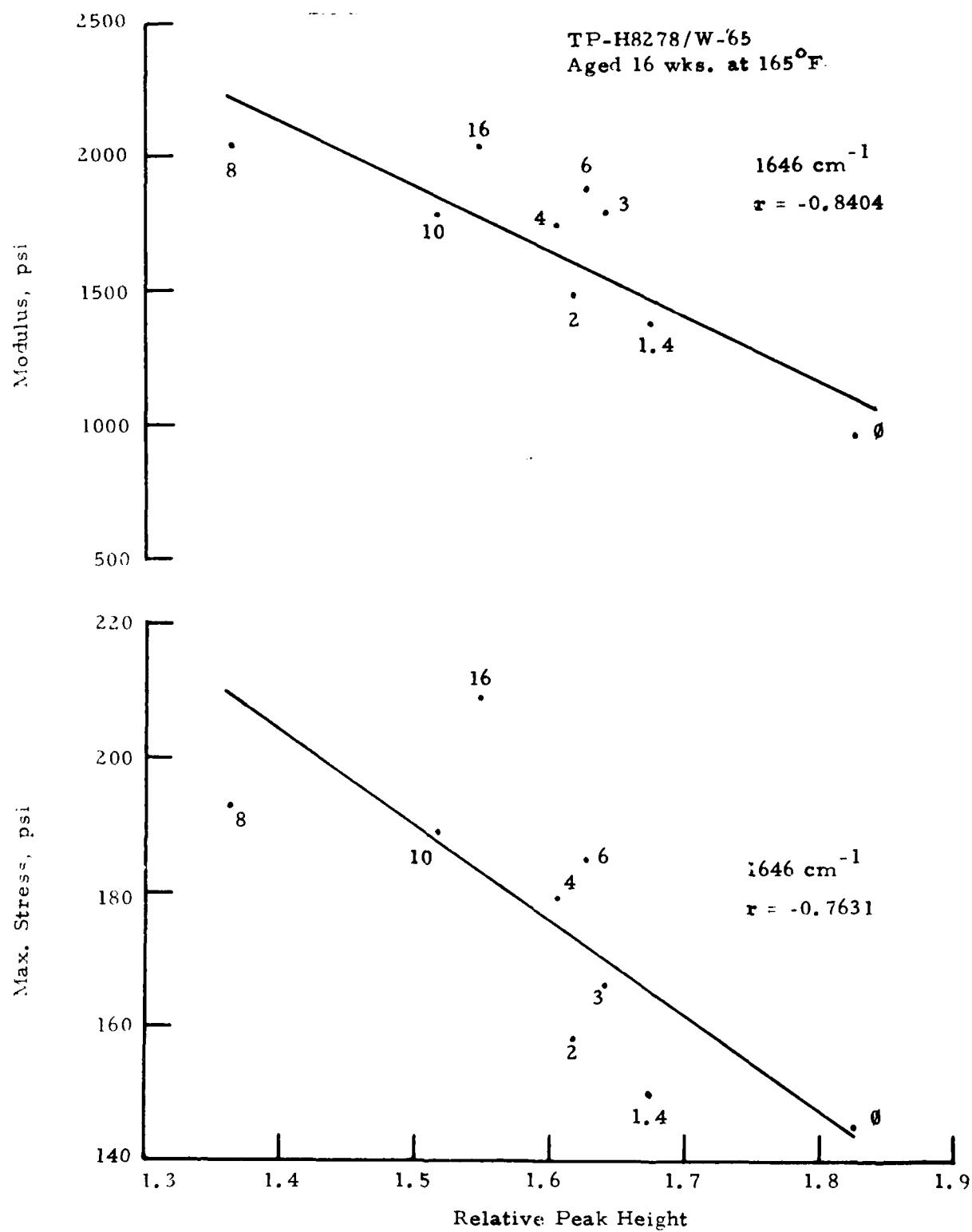
Figure G-2. Correlation of Stress and Modulus with Peak Height at 1646 cm^{-1}.

Calculation of correlation coefficients for changes in peak heights of propellant aged at 145°F revealed that the peak occurring at 1646 cm^{-1} correlated quite well with maximum stress and modulus. There was also a high correlation for the peak occurring at 965 cm^{-1}. This peak, however, resides on the side of the large ammonium perchlorate absorption occurring near 1050 cm^{-1}, and, because of the influence of ammonium perchlorate on this peak, it was felt those data were somewhat in question and the correlation coefficient might be an artifact of some uncontrolled phenomenon. Correlation coefficients for the 145°F aging temperature shown in Table G-1 require a correlation coefficient of 0.669 for a 90% confidence level. Changes in the height of the peak at 1646 cm^{-1} were plotted against maximum stress and modulus; these plots are shown on Figure G-3.

All of the 145° and 165°F mechanical property data and infrared spectral data were treated as a single set of data; i.e., the 8 data points for aging at 165°F and the 6 data points for aging at 145°F were combined with the zero-time aging data and all 15 data points treated as a single unit. A statistical analysis was performed to find if there were simple correlations or multiple correlations of spectral peak height changes with mechanical property changes for the two combined aging temperatures. With 15 data points, a correlation coefficient of 0.514 is required for the 95% confidence level and a correlation coefficient of 0.641 is needed for a confidence level of 99%. A number of correlations were found which surpassed the 95% confidence level. For the simple correlations these coefficients were calculated:

Peak at 2852 versus strain	0.6046
Peak at 1646 versus peak at 1313	0.5401
Peak at 1646 versus modulus	-0.7306
Peak at 1646 versus stress	-0.6607
Peak at 1514 versus peak at 1236	0.6732
Peak at 1236 versus modulus	-0.5249
Peak at 965 versus peak at 911	0.9238

Only those changes of infrared peak height versus mechanical properties were given consideration. Changes of one infrared peak with a second infrared peak, whether a positive or negative correlation, were not given further consideration. Changes in the 1646 cm^{-1} peak with modulus and stress correlated quite well, having correlation coefficients of -0.7306 and -0.6607, respectively. These changes are plotted on Figure G-4. Note on that figure that there are a few "outliers" in each of the plots but overall the correlation is very good, particularly considering the fact that there are 15 data points with the data taken at two different temperatures.
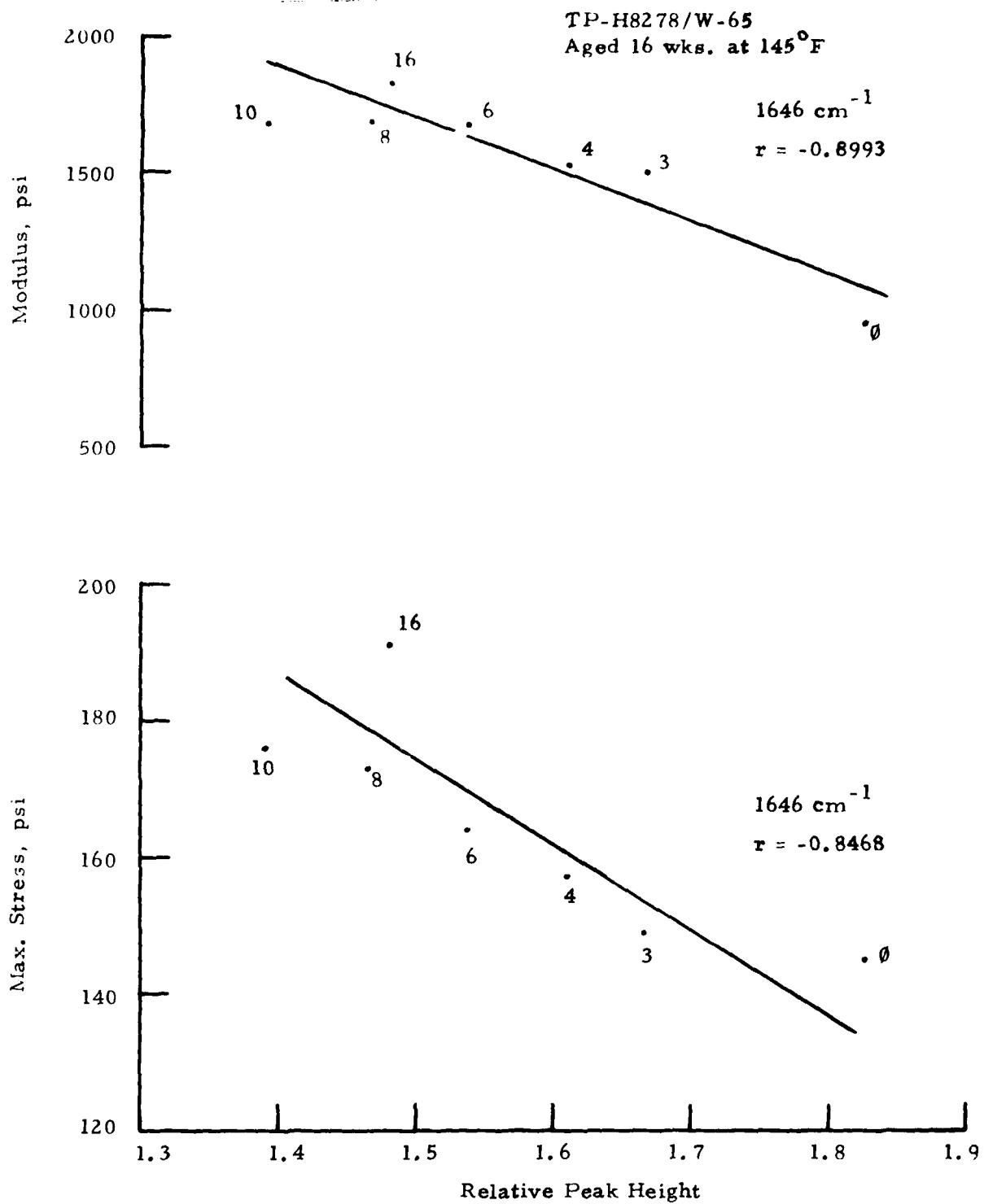
Figure G-3. Correlation of Stress and Modulus with Peak Height Changes at 1646 cm^{-1}.

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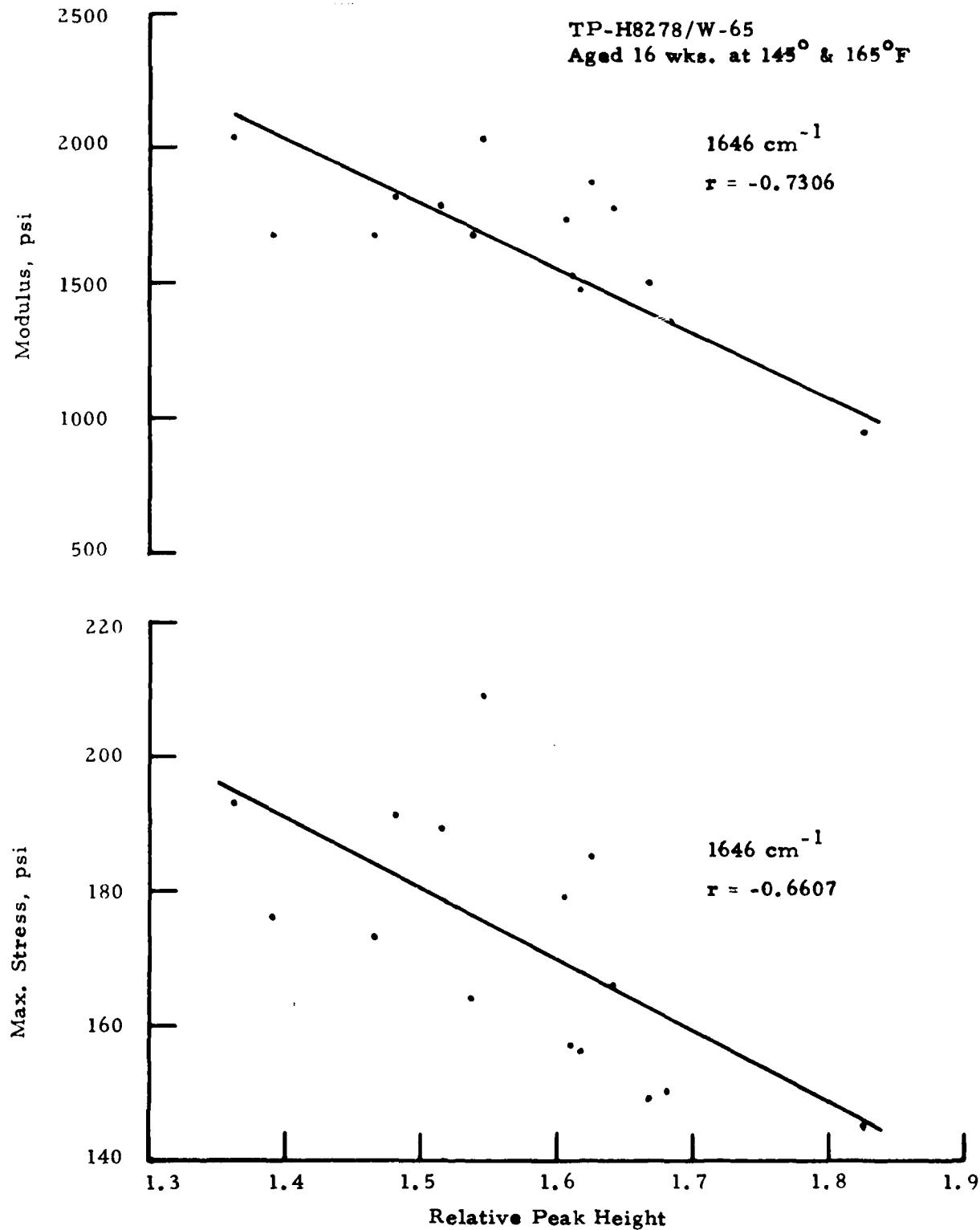
Figure G-4. Correlation of Stress and Modulus with Peak Height Changes at 1646 cm^{-1}.

A computer program was used to generate the simple correlation coefficients reported above, and it also computed two multiple correlations. It was found that, when the peak at 1646 cm^{-1} and the peak at 1236 cm^{-1} were combined, a strong correlation existed with modulus and an only slightly less strong correlation existed with maximum stress. Correlation equations computed for these were as follows:

Modulus = 8196 - 1515 (peak ht. at 1646) - 1345 (peak ht. at 1236)

Stress = 583.6 - 92.86 (peak ht. at 1646) - 85.87 (peak ht. at 1236)

The coefficient for the modulus parameter was determined to be 0.8300. With 15 data points, a confidence level of 99% requires a correlation coefficient of 0.732. The correlation coefficient for the stress parameter was 0.7568 and here, again, for a confidence level of 99%, the correlation coefficient must be 0.732. Both of these correlations are considered to be quite strong. For the modulus correlation, the standard error of estimate was 166.4 with a coefficient of variation equal to 10%. For the stress correlation, the standard error of estimate was 13.29 psi with a coefficient of variation of 7.71%.

AP-LEACHED PROPELLANT

Propellant employed here was TP-H8278, Mix W-65 aged at 165°F and tested at the following time periods: 0, 1.4, 2, 3, 4, 6, 8, 10, and 16 weeks.

Ammonium perchlorate was leached from the propellant using the standard procedure in which the samples were submerged in running water at 35 to 40°C for a period of 24 hours. Samples were then dried at 60°C for 4 hours and then at room temperature over night. Infrared spectra of the propellant were run using the Barnes ATR unit and the standard procedures that have been reported in the body of this report under Phase I. Following the reduction of the infrared data by the computer program, where normalization was accomplished at 2920 cm^{-1}, the peak height information was input to a statistical regression analysis program where the heights of 13 peaks were selected as independent variables and three mechanical properties, modulus, stress, and strain, were employed as dependent variables. This computer program calculates simple correlations for all possible combination of all dependent and independent variables and then performs a multiple regression analysis to establish an equation which represents the magnitude of each of the three mechanical properties as a function of the most influential infrared spectral peaks. The number of peaks selected for inclusion in the equation is based upon their influence or relationship to changes in the mechanical property being examined.

A typical IR spectrum of TP-H8278 with AP removed by water leaching is shown on Figure G-5.
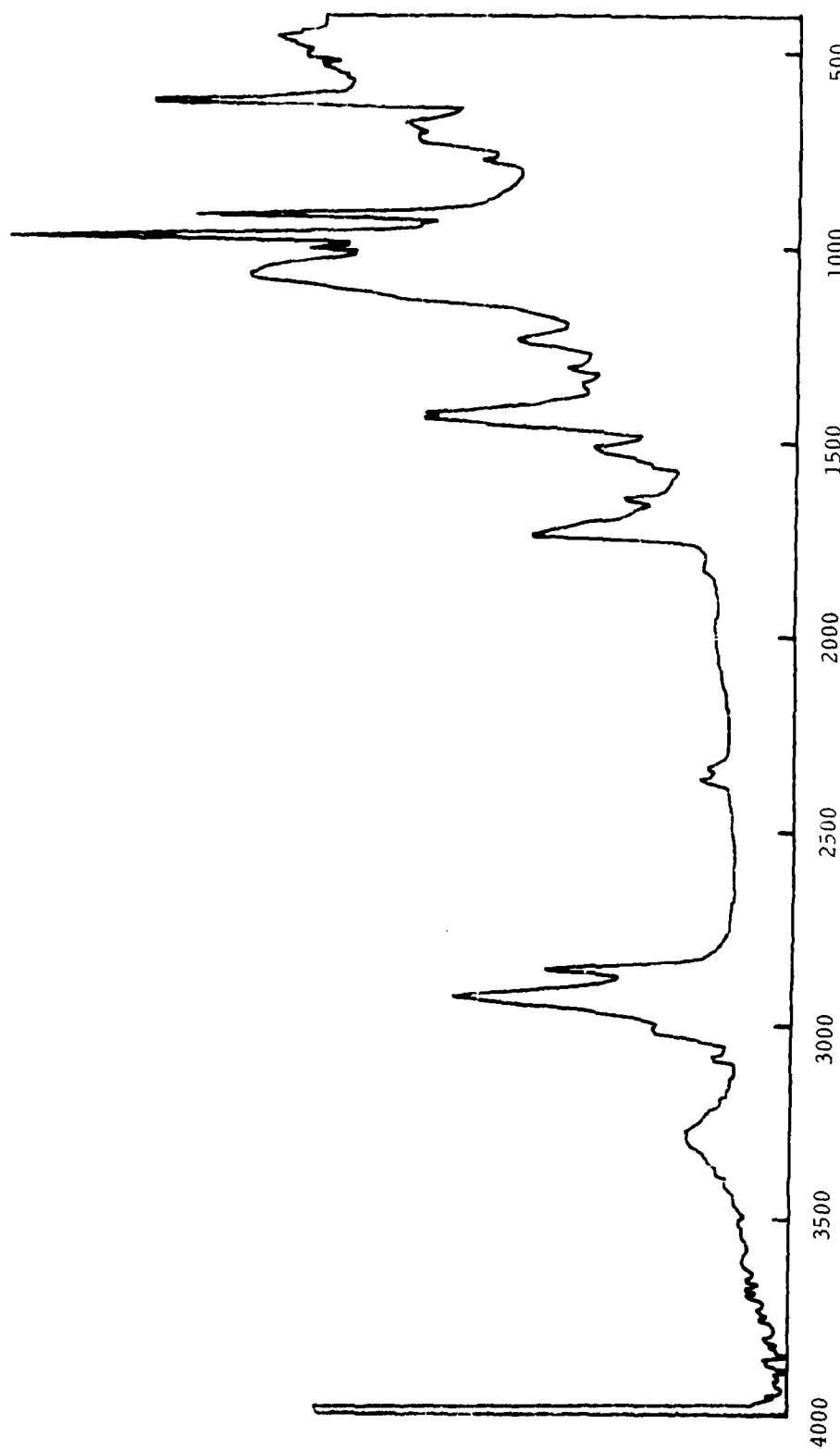
Figure G-5. Typical IR Spectrum of TP-H8278/W-65 with AP Removed by Water Leaching (Propellant Aged, Zero Time).

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Simple correlations between peak height changes and mechanical property changes that were found are displayed in Table G-2. Four correlations were found with modulus and three were found with strain. No correlations of significance were found with stress. Those correlation which have a value greater than 0.80 are statistically significant at the 99% level while those having correlation coefficients of less than that value, but greater than 0.67 are statistically significant at the 95% level.

Multiple correlations concerning modulus, stress and strain are displayed in Tables G-3, G-4, and G-5 respectively. The correlation between peak height changes and modulus was an equation that contained six terms, leaving three degrees of freedom. The multiple correlation coefficient for this equation, however, was 0.9995 and thus it is statistically significant at the 99% level. It is interesting to note that the standard error of estimate going in to this equation was 353.3 psi and applying this equation the standard error of estimate is reduced to approximately 18 psi. A plot of modulus calculated from this equation and measured modulus is displayed on Figure G-6.

The multiple correlation concerning stress involved four terms leaving five degrees of freedom; and the correlation coefficient for this equation was 0.9755 meaning that it is statistically significant at the 99% level. The standard error of estimate going in was 21.47 psi while after applying the equation the standard error of estimate is reduced to 5.97 psi. A plot of stress as calculated using the equation shown on Table G-4 against measured stress is displayed on Figure G-7.

The correlation of peak height changes with changes in strain resulted in a multiple correlation having two terms in the equation thus giving seven degrees of freedom. The correlation coefficient for this equation is 0.8248 which means that it is statistically significant at the 99% level. A plot of strain as calculated from the equation against measured strain is displayed on Figure G-8.

TABLE G-2

SIMPLE CORRELATIONS OF PEAK HEIGHT CHANGES

AND MECHANICAL PROPERTY CHANGES

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, AP leached propellant)

Peak, cm^{-1}	Correlation Coefficient for Mechanical Properties		
	Modulus	Stress	Strain
1738	-0.8289		0.7588
1514	0.7573		-0.8248
1352	0.7617		-0.6942
965	0.7723		

For 9 observations (no. of age time tests):

$R_{.95} = 0.67$

$R_{.99} = 0.80$

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TABLE G-3

MULTIPLE CORRELATIONS FOR PEAK HEIGHT

CHANGES AND MODULUS

(TP-H8278/W-65, Aged 0 to 16 Wks at $165^\circ F$, AP leached)

$$MODULUS = -945.6 + 312.9 (X_4) - 93.03 (X_5) + 707.8 (X_6) - 2754 (X_8) + 22.26 (X_{11})$$

Where: X_4 = peak height at 1738 cm^{-1}
X_5 = peak height at 1646 cm^{-1}
X_6 = peak height at 1514 cm^{-1}
X_8 = peak height at 1305 cm^{-1}
X_{11} = peak height at 965 cm^{-1}

$R = 0.9995$
$R^2 = 0.9990$

Standard Deviation Going In = 353.3 psi

Standard Error of Estimate w/Equation = 18.61 psi

For 9 observations and 3 degrees of freedom: $R_{.99} = 0.99$

MULTIPLE CORRELATIONS FOR PEAK HEIGHT

CHANGES AND STRESS

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, AP leached)

STRESS $= 840.9 + 111.6 \ (X_7) - 153.1 \ (X_8) - 8.843 \ (X_{12})$

Where: X_7 = peak height at 1352 cm^{-1}

X_8 = peak height at 1305 cm^{-1}

X_{12} = peak height at 911 cm^{-1}

$R = 0.9755$

$R^2 = 0.9517$

Standard Error of Estimate Going In = 21.47 psi

Standard Error of Estimate w/Equation = 5.97 psi

For 9 observations and 5 degrees of freedom: $R_{.99} = 0.917$

TABLE G-5

MULTIPLE CORRELATIONS FOR PEAK HEIGHT

CHANGES AND STRAIN

(TP-H8278/W-65, Aged 0 to 16 Wks at 165°F, AP leached)

STRAIN = 38.87 - 2.549 (X_6)

Where: X_6 = height of peak at 1514 cm^{-1}

R = 0.8248

R^2 = 0.6804

Standard Error of Estimate Going In = 1.658% Strain

Standard Error of Estimate w/Equation = 1.002% Strain

For 9 observations and 7 degrees of freedom: $R_{.99}$ = 0.80

TP-H8278/W-65
Aged 0 → 16 Wk at 165°F
AP leached w/H₂O

R = 0. ----
R.99 = 0.99
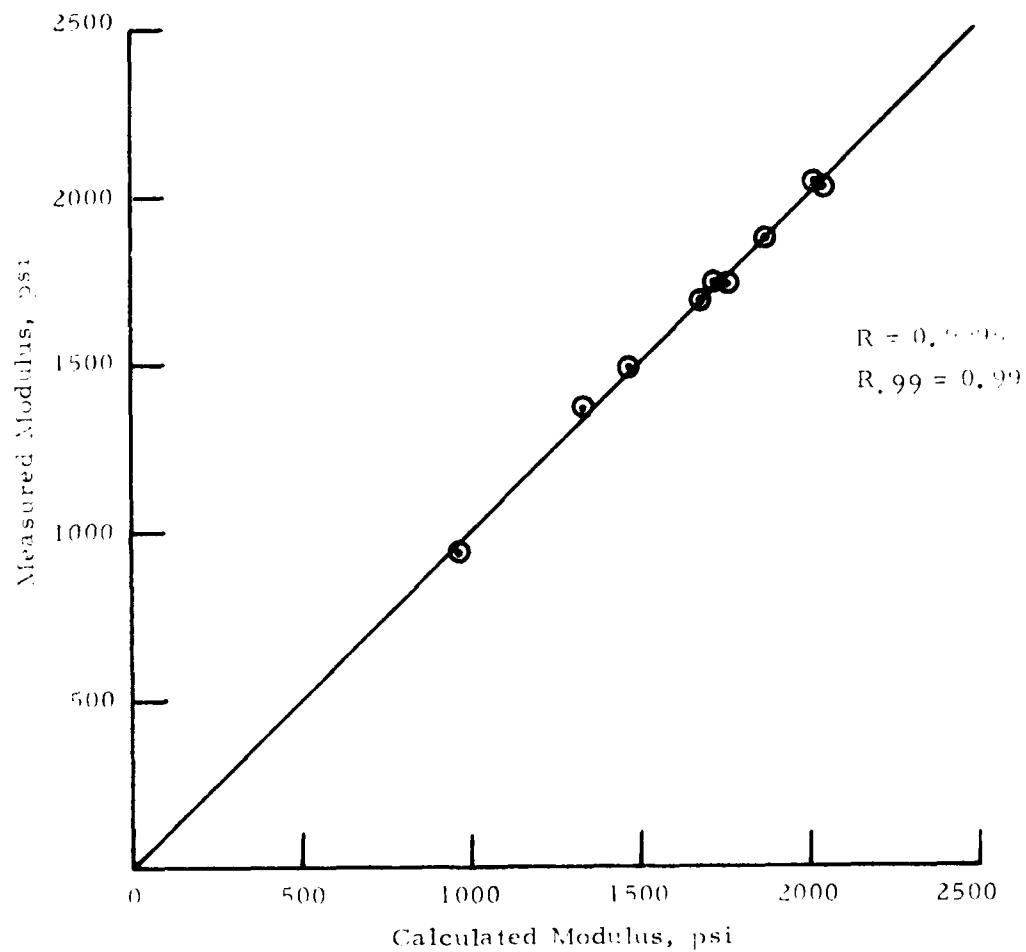
Figure G-6. Multiple Correlation for Modulus.

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TP-H8278/W-65
Aged 0→16 wk at 165°F
AP leached w/H₂O

R = 0.9755
R.99 = .917
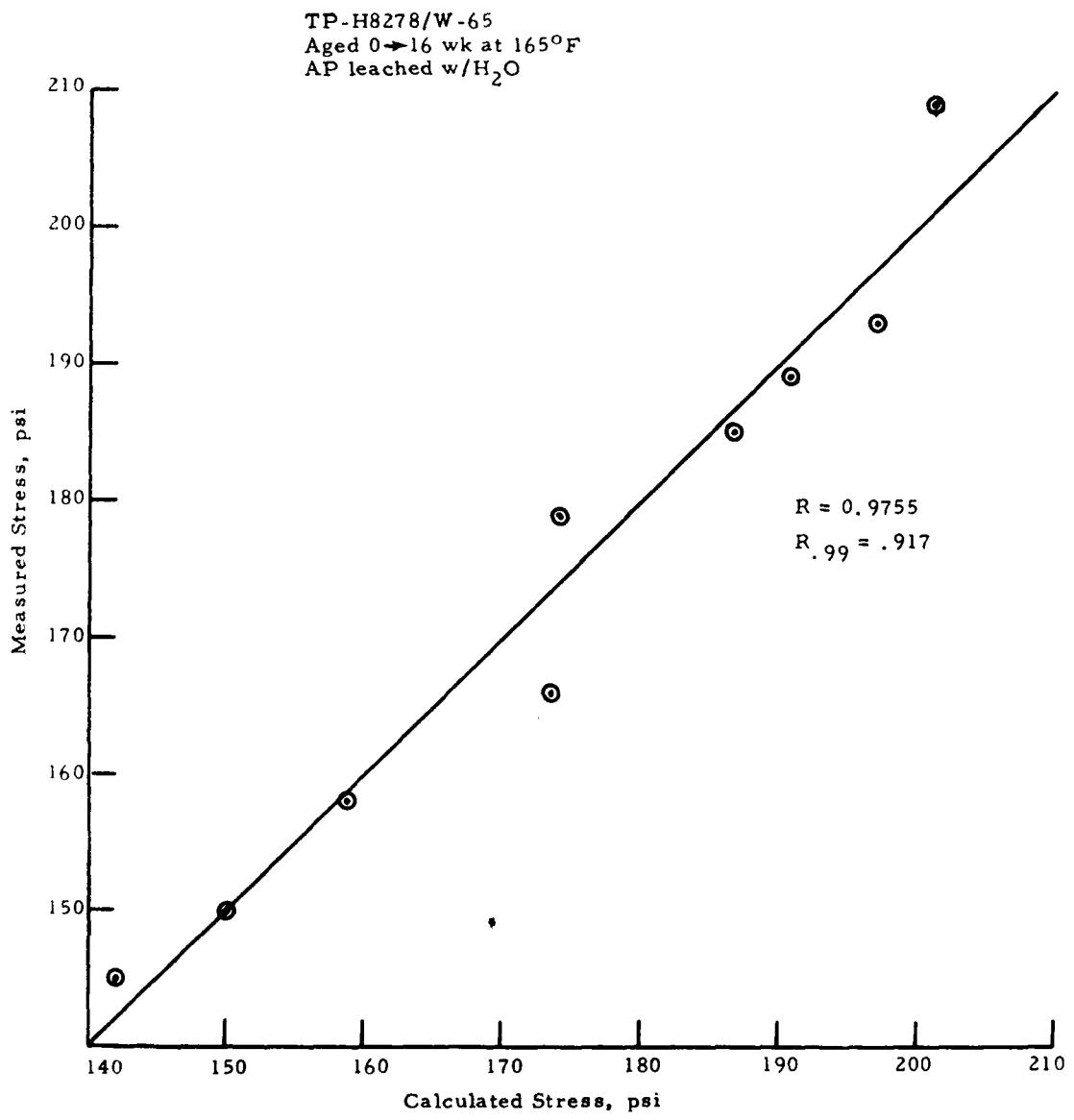
Figure G-7. Multiple Correlation for Stress.

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TP-118278/W-65
Aged 0 →16 Wk. at 165°F
AP leached w/H_2O

R = 0.8248
$R_{.99}$ = 0.80
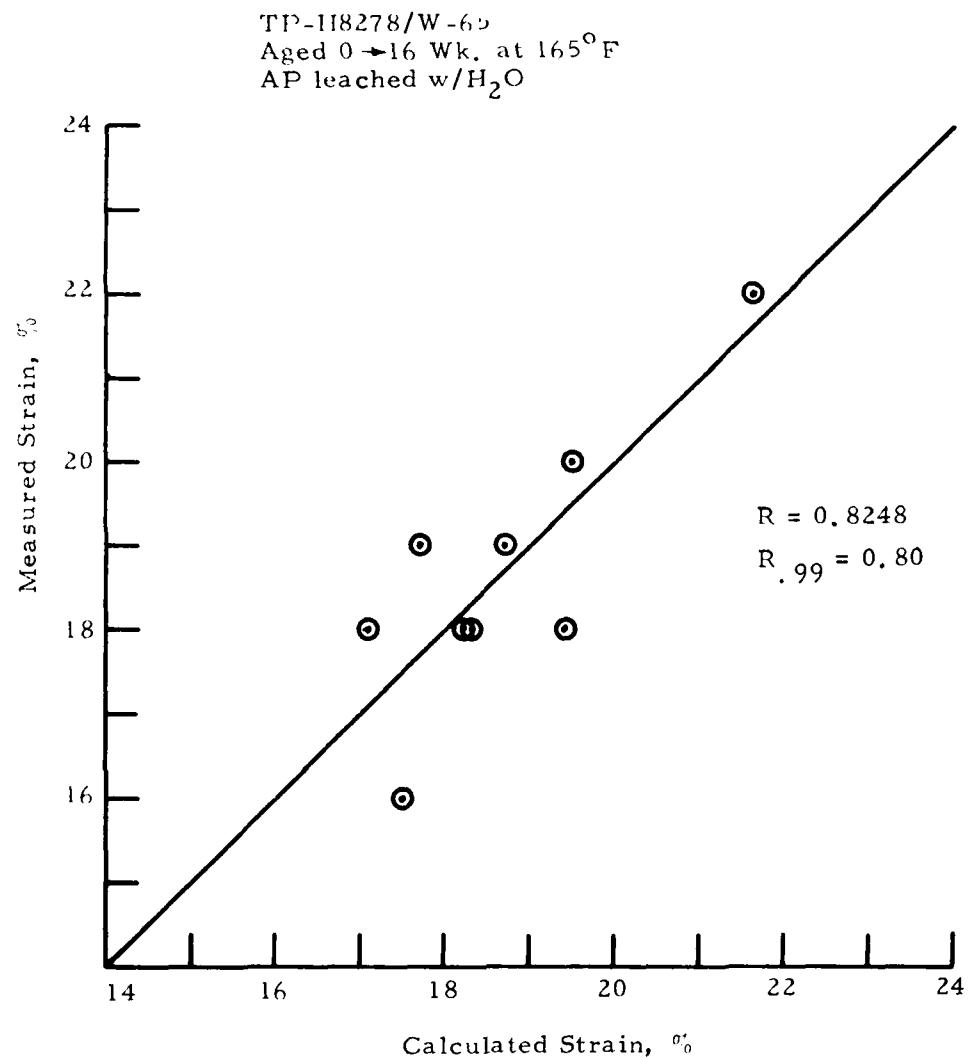
Figure G-8. Multiple Correlation for Strain.

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CONCLUSIONS

1) Changes in the IR spectra of the binder of TP-H8278 propellant correlate well with changes in the mechanical properties of the propellant as the propellant ages.

2) Whether the propellant IR spectra are made of whole propellant or AP-leached propellant does not affect the existance of correlations between the spectral changes and mechanical property changes.

3) AP-leached and whole propellant do not have the same correlating peaks.

4) In order to establish the correlation between IR peak changes and mechanical property changes, all samples of propellant in the aging program must be treated in exactly the same way throughout the aging program.